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AND

WILLIAM FRANCIS, Ph.D. F.L.S. F.R.A.S. F.C.S.

" Nec aranearum sane textus ideo melior quia ex se fila gignunt, nec noster vilior quia ex alienis libamus ut apes." Just. Lips. *Polit.* lib. i. cap. 1. Not.

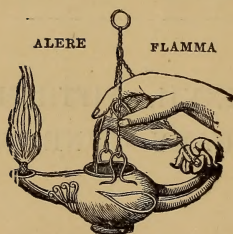## VOL. XXXVII.—FIFTH SERIES.
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"Meditationis est perscrutari occulta; contemplationis est admirari perspicua .... Admiratio generat quæstionem, quæstio investigationem, investigatio inventionem."—*Hugo de S. Victore.*

———"Cur spirent venti, cur terra dehiscat,
Cur mare turgescat, pelago cur tantus amaror,
Cur caput obscura Phœbus ferrugine condat,
Quid toties diros cogat flagrare cometas,
Quid pariat nubes, veniant cur fulmina cœlo,
Quo micet igne Iris, superos quis conciat orbes
Tam vario motu."

J. B. Pinelli ad Mazonium.

ALERE FLAMMA

CONTENTS OF VOL. XXXVII.

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ERRATUM.

Page 487, line 10 from top, *for* not far removed from *read* not even distantly related to.

PLATES.

I. *Note on the Generalizations of* Van der Waals *regarding "Corresponding" Temperatures, Pressures, and Volumes. By* Sydney Young, *D.Sc., F.R.S., Professor of Chemistry, University College, Bristol* [*].

IN a paper read before the Physical Society in November 1891, and published under the above title in the Philosophical Magazine for February 1892 (xxxiii. p. 153), the absolute temperatures and the molecular volumes (as liquid and saturated vapour) of eleven compounds were compared with those of fluorbenzene at a series of corresponding pressures.

It was pointed out, however (p. 155), that a better mode of procedure in many respects would have been to give the temperatures, pressures, and volumes of each of the twelve substances in terms of its critical constants; but as the critical volumes of several of the compounds had not been directly determined, and as none of them were known with accuracy, the method had to be abandoned.

Since then it has been shown by M. Mathias that the critical densities—and therefore the volumes—may be determined with great accuracy by the method of Cailletet and

Mathias, and as the values calculated by M. Mathias differed very slightly from those obtained independently by the same method by myself, I accepted these values as correct (Phil. Mag. Dec. 1892). It appears, however, that there were a few small errors in the calculations, and I have therefore adopted my own values in the tables that follow. The new critical molecular volumes and those previously accepted as correct are given below ; it will be seen that the alterations are very small.

Substance.	Critical Molecular Volume.		Substance.	Critical Molecular Volume.	
	Old.	Corrected.		Old.	Corrected.
Fluorbenzene............	270·4	270·5	Stannic chloride .	349·3	350·4
Chlorobenzene	306·5	305·7	Ether	280·7	281·4
Bromobenzene	322·4	321·4	Acetic acid.........	170·3	170·5
Iodobenzene	348·4	347·9	Methyl alcohol ...	118·0	118·0
Benzene	256·3	256·3	Ethyl alcohol ...	166·9	166·9
Carbon tetrachloride .	276·1	275·6	Propyl alcohol ...	217·6	217·6

The vapour-pressures, molecular volumes, and critical constants of ten esters [methyl formate, acetate, propionate, butyrate, and isobutyrate ; ethyl formate, acetate, and propionate ; propyl formate and acetate] have recently been determined by Mr. G. L. Thomas and myself, and the absolute temperatures, pressures, and volumes of each substance have been given in terms of its critical constants (Trans. Chem. Soc. lxiii. p. 1191).

In order to allow of a comparison being made, pressures "corresponding" with the previous ones (with a few omissions) were taken, and I now propose to give the absolute temperatures and volumes of the substances previously studied in terms of their critical constants. As the data for the esters are published in full in the Trans. Chem. Soc., it is unnecessary to reproduce them here, and it will be sufficient to give the extreme values for the ten esters in each case.

Ratios of Boiling-Points (Abs. temps.) at Corresponding Pressures to Absolute Critical Temperatures.

Pressures C₆H₅F.	Fraction of Critical Pressure.	C₆H₅F.	C₆H₅Cl.	C₆H₅Br.	C₆H₅I.	C₆H₆.	CCl₄.	SnCl₄.	(C₂H₅)₂O	CH₃OH.	C₂H₅OH.	C₃H₅.OH	CH₃COOH	Ten Esters.
20	·00059	·4866	·4870	·4870	·4872	·4795	·4748	·4914	...	·5374	·5536	·5579	·5164	·4976 to ·5172
50	·00147	·5170	·5172	·5169	·5170	·5098	·5053	·5216	...	·5685	·5836	·5861	·5478	·5189 „ ·5468
100	·00295	·5431	·5429	·5427	·5427	·5359	·5313	·5471	...	·5943	·6085	·6101	·5743	·5447 „ ·5718
200	·00590	·5723	·5723	·5717	·5717	·5648	·5608	·5763	·5777	·6229	·6361	·6365	·6041	·5740 „ ·5599
400	·01180	·6054	·6052	·6049	·6049	·5989	·5943	·6089	·6097	·6550	·6665	·6656	·6372	·6070 „ ·6314
760	·02241	·6400	·6402	·6403	·6401	·6334	·6293	·6435	·6444	·6882	·6981	·6960	·6716	·6413 „ ·6650
1500	·04423	·6827	·6833	·6833	·6830	·6765	·6728	·6855	·6866	·7277	·7355	·7326	·7133	·6838 „ ·7059
3000	·08846	·7334	·7345	·7343	·7337	·7282	·7251	·7357	·7371	·7734	·7794	·7736	·7624	·7348 „ ·7541
5000	·14740	·7771	·7786	·7777	...	·7725	·7697	·7788	·7798	·8119	·8161	·8118	·8081	·7778 „ ·7949
7000	·20640	·8092	·8103	·8090	...	·8052	·8025	·8106	·8113	·8396	·8429	·8384	·8322	·8101 „ ·8248
10000	·29490	·8464	·8466	...	...	·8429	·8411	·8463	·8472	·8708	·8738	·8690	·8651	·8452 „ ·8595
15000	·44230	·8930	·8926	...	...	·8906	·8889	·8934	·8923	·9098	·9119	·9082	·9057	·8915 „ ·9028
20000	·58990	·9288	·9285	...	...	·9270	·9260	·9287	·9277	·9381	·9412	·9383	·9368	·9279 „ ·9357
25000	·73720	·9579	·9576	...	...	·9566	·9565	·9577	·9573	·9643	·9652	·9637	·9626	·9574 „ ·9624
28000	·82570	·9731	·9727	...	...	·9725	·9725	·9732	·9728	·9775	·9775	·9771	·9740	·9729 „ ·9762
30000	·88460	·9829	·9826	...	...	·9824	·9822	·9829	·9824	·9855	·9856	·9857	·9844	·9827 „ ·9847
32000	·94360	·9919	·9916	...	...	·9915	·9917	·9916	·9915	·9929	·9931	·9934	·9926	·9918 „ ·9928
33912	1·00000	1·0000	1·0000	1·0000	1·0000	1·0000	1·0000	1·0000	1·0000	1·0000	1·0000	1·0000	1·0000	1·0000 „ 1·0000

Ratios of Volumes of Liquid at Corresponding Pressures to Critical Volumes.

Pressures C_6H_5F.	Fraction of Critical Pressure.	C_6H_5F.	C_6H_5Cl.	C_6H_5Br.	C_6H_5I.	C_6H_6.	CCl_4.	$SnCl_4$.	$(C_2H_5)_2O$	CH_3OH.	C_2H_5OH.	C_3H_7OH.	CH_3COOH	Ten Esters.
20	·00059	·3381	·3366	·3360	·3357	·3359	...	·3314	...	...	·3446	·3393	·3292 to ·3324
50	·00147	·3449	·3431	·3424	·3421	·3428	·3444	·3387	...	·3413	·3501	·3460	·3358 ,, ·3392
100	·00295	·3508	·3488	·3482	·3480	·3489	·3505	·3447	...	·3455	·3552	·3523	·3419 ,, ·3451
200	·00590	·3578	·3557	·3551	·3550	·3560	·3574	·3519	...	·3522	·3626	·3610	·3597	·3490 ,, ·3523
400	·01180	·3661	·3641	·3635	·3635	·3648	·3660	·3611	·3631	·3596	·3698	·3679	·3686	·3576 ,, ·3608
760	·02241	·3755	·3737	·3732	·3732	·3742	·3756	·3705	·3729	·3680	·3781	·3759	·3788	·3671 ,, ·3704
1500	·04423	·3885	·3867	·3862	·3863	·3870	·3889	·3838	·3859	·3793	·3893	·3870	·3924	·3807 ,, ·3836
3000	·08846	·4067	·4046	·4041	·4042	·4053	·4072	·4021	·4033	·3949	·4047	·4028	·4106	·3992 ,, ·4021
5000	·14740	·4250	·4228	·4222	...	·4233	·4251	·4199	·4209	·4104	·4223	·4193	·4284	·4176 ,, ·4205
7000	·20640	·4404	·4386	·4380	...	·4389	·4402	·4356	·4368	·4243	·4367	·4340	·4439	·4334 ,, ·4364
10000	·29490	·4622	·4603	...	...	·4602	·4623	·4575	·4596	·4438	·4563	·4550	·4655	·4552 ,, ·4683
15000	·44230	·4977	...	...	...	·4960	·4983	·4948	·4948	·4760	·4891	·4897	·5003	·4912 ,, ·4940
20000	·58990	·5363	...	...	...	·5353	·5377	·5346	·5324	·5131	·5286	·5280	·5387	·5305 ,, ·5354
25000	·73720	·5855	...	...	...	·5845	·5874	...	·5833	·5601	·5772	·5775	·5871	·5800 ,, ·5855
28000	·82570	·6260	...	...	...	·6250	·6297	...	·6261	·6010	·6147	·6177	·6302	·6200 ,, ·6254
30000	·88460	·6631	...	...	...	·6613	·6654	...	·6628	·6359	·6537	·6550	·6651	·6559 ,, ·6633
32000	·94360	·7134	...	...	...	·7113	·7121	...	·7171	·6906	·7070	·7077	·7144	·7099 ,, ·7204
33912	1·00000	1·0000	1·0000	1·0000	1·0000	1·0000	1·0000	1·0000	1·0000	1·0000	1·0000	1·0000	1·0000	1·0000 ,, 1·0000

Ratios of Volumes of Saturated Vapour at Corresponding Pressures to Critical Volumes.

Pressures C_6H_5F.	Fraction of Critical Pressure.	C_6H_5F.	C_6H_5Cl.	C_6H_5Br.	C_6H_5I.	C_6H_6.	CCl_4.	$SnCl_4$.	$(C_2H_5)_2O$	CH_3OH.	C_2H_5OH.	C_3H_7OH.	CH_3COOH.	Ten Esters.
20	·00059	...	...	...	...	...	...	...	...	...	...	...	2290	...
50	·00147	...	...	...	...	...	...	...	...	...	...	...	1010	...
100	·00295	...	...	...	...	...	...	...	...	891	825	...	549	...
200	·00590	...	...	...	...	...	...	...	...	463	429	...	298	...
400	·01180	...	...	...	...	...	...	...	192	239	223	221	127	...
760	·02241	...	...	...	...	...	...	...	105	130	121	119	90·3	...
1500	·04423	55·5	55·3	54·8	55·1	54·4	52·8	54·6	55·2	67·3	62·9	61·6	48·5	56·9 to 59·4
3000	·08846	28·4	28·65	28·4	28·45	28·2	27·4	28·1	28·3	34·2	32·1	31·1	25·5	29·2 „ 30·3
5000	·14740	17·15	17·35	17·25	...	17·25	16·75	16·95	17·1	20·4	19·3	18·6	15·7	17·4 „ 18·45
7000	·20640	12·2	12·35	12·30	...	12·35	11·95	12·1	12·15	14·4	13·65	13·15	11·3	12·5 „ 13·1
10000	·29490	8·37	8·43	...	...	8·49	8·19	8·41	8·38	9·82	9·33	9·01	7·91	8·56 „ 8·92
15000	·44230	5·35	...	...	...	5·35	5·23	5·25	5·36	6·17	5·76	5·52	5·16	5·41 „ 5·57
20000	·58990	3·73	...	...	...	3·72	3·67	3·64	3·74	4·23	3·90	3·84	3·68	3·73 „ 3·85
25000	·73720	2·71	...	...	...	2·69	2·66	...	2·70	2·98	2·80	2·73	2·68	2·69 „ 2·78
28000	·82570	2·22	...	...	...	2·20	2·17	...	2·21	2·40	2·31	2·25	2·20	2·21 „ 2·28
30000	·88460	1·91	...	...	...	1·91	1·88	...	1·93	2·08	1·99	1·96	1·91	1·91 „ 1·95
32000	·94360	1·63	...	...	...	...	1·62	...	1·61	1·76	1·65	1·69	1·62	1·61 „ 1·64
33912	1·00000	1·00	1·00	1·00	1·00	1·00	1·00	...	1·00	1·00	1·00	1·00	1·00	1·00 „ 1·00

It was pointed out in the earlier paper on this subject (Phil. Mag. xxxiii. p. 172) that the compounds investigated might be arranged in groups, and this is confirmed by the method of comparison now adopted. The twenty-two compounds appear to fall into four chief groups :—

I. Benzene and its halogen derivatives, carbon tetrachloride, stannic chloride, ether.

II. The three alcohols (methyl alcohol differing, however, considerably from the others).

III. Acetic acid.

IV. The ten esters.

Ratios of Absolute Temperatures at Corresponding Pressures to Absolute Critical Temperatures.—The ratios for the compounds in groups I. are the lowest ; those for the esters are mostly higher; acetic acid comes next in order; whilst the values for the alcohols are much higher than for any of the other substances.

In the first group the differences are not great, but the ratios for benzene and carbon tetrachloride are below, and those for stannic chloride and ether at low pressures are somewhat above the average. The influence of molecular weight and constitution on the ratios for the esters is fully discussed in the paper by Mr. Thomas and myself (Trans. Chem. Soc. lxiii. p. 1252), and it will be sufficient here to mention that there is a marked rise as the molecular weight increases. This is not the case, however, with the ratios of the volumes of liquid or of saturated vapour to the critical volumes. All the ratios appear to depend to some extent on the constitution of the esters.

Ratios of Volumes of Liquid at Corresponding Pressures to Critical Volumes.—The differences in this case are small ; in general the ratios for acetic acid are the highest, and those for the esters the lowest. At the lowest pressures the values for the alcohols are higher than for the esters, but at high pressures they are lower than for any of the other substances, and this is especially the case with methyl alcohol.

Ratios of Volumes of Saturated Vapour at Corresponding Pressures to Critical Volumes.—The grouping of the compounds is well seen in this case, the differences being naturally most marked at low pressures. Acetic acid stands quite alone with the lowest ratios, whilst the alcohols, and especially methyl alcohol, have much higher ratios than the other compounds. Of the remaining substances the esters have higher values than the members of the first group.

There is little doubt that the low ratios for acetic acid are due to the existence of complex molecules in the saturated

vapour at low temperatures. The densities of the saturated vapours of the alcohols, on the other hand, are normal at low temperatures, and complex molecules cannot, therefore, be present; but there is considerable evidence of their existence in the liquid state.

Ramsay and Shields (Phil. Trans. 184 A. p. 647 ; Trans. Chem. Soc. lxiii. p. 1089) have recently studied the surface-energy of a large number of compounds, and have described a method by which the molecular complexity of liquids may be ascertained. They show that most of the liquids investi-gated have the same molecular weight in the liquid as in the gaseous state, but that there is greater molecular complexity in the liquid state in the case of the fatty acids and alcohols. As regards homologous compounds—both acids and alcohols—the complexity diminishes with rise of molecular weight, and as regards individual compounds it diminishes with rise of temperature; in order of complexity methyl alcohol comes next to acetic acid.

These conclusions, based on totally different considerations, agree perfectly with those suggested in this paper and in the previous one on the same subject.

An explanation of the relatively high molecular volumes of the saturated vapour of the alcohols at low temperatures would be afforded by the assumption that complex molecules exist to some extent at the critical points, an assumption which is supported by the high critical densities.

It has been shown (Phil. Mag. Nov. 1890, p. 423) that if the generalizations of Van der Waals were strictly true, the following relation should be true for all substances :—

$$\frac{v}{v'} = \frac{V}{V'} = \frac{T}{T'} \times \frac{p'}{p},$$

where v and v' are the molecular volumes of saturated vapour, V and V' those of liquid, and T and T' the boiling-points on the absolute scale of temperature of any two substances at corresponding pressures p and p'. This relation should hold good at the critical point, or

$$\frac{PV}{T} = \text{constant},$$

where P, V, and T are the critical pressure, the critical molecular volume, and the absolute critical temperature of any substance. As the critical volumes are now known, it is possible to test this relation at the critical points of the various com-pounds, and the values of $\frac{PV}{T}$ are given in the table below.

Again, the ratios of the actual to the theoretical density (for a perfect gas) at the critical point should be the same for all substances if Van der Waals's generalizations were strictly true : these ratios are also given in the table under the heading $\frac{D}{D'}$.

Substance.	$\frac{PV}{T}$.	$\frac{D}{D'}$.
Fluorbenzene	16390	3·79
Chlorobenzene	16380	3·77
Bromobenzene	16270	3·80
Iodobenzene	16360	3·78
Benzene	16610	3·71
Carbon tetrachloride...	16940	3·65
Stannic chloride	16630	3·76
Ether	16290	3·83
Methyl alcohol	13750	4·52
Ethyl alcohol	15470	4·02
Propyl alcohol	15460	4·02

Substance.	$\frac{PV}{T}$.	$\frac{D}{D'}$.
Acetic acid	12440	5·00.
Methyl formate	15840	3·93
Ethyl formate	15990	3·88
Methyl acetate	15750	3·94
Propyl formate	16070	3·87
Ethyl acetate	15730	3·95
Methyl propionate	15920	3·90
Propyl acetate	15760	3·94
Ethyl propionate	15830	3·92
Methyl butyrate	15900	3·90
Methyl isobutyrate	16070	3·87

Here, again, the grouping of the compounds is well marked : acetic acid has by far the lowest value of $\frac{PV}{T}$ (and the highest density ratio) ; the alcohols come next in order, the values for methyl alcohol standing about midway between those for the other alcohols and acetic acid ; the esters agree well together, the values of $\frac{PV}{T}$ being in every case lower than for the members of the first group.

II. *On the Separation of Three Liquids by Fractional Distillation. By* Professor F. R. BARRELL, *M.A., B.Sc.,* G. L. THOMAS, *B.Sc., and* Professor SYDNEY YOUNG, *D.Sc., F.R.S., University College, Bristol* [*].

IT is well known that the separation by fractional distillation of two substances which are miscible in all proportions and which do not—like propyl alcohol and water or formic acid and water—form mixtures of constant boiling-point, is usually a simple matter if there is a considerable difference in their boiling-points. The facility with which the separation can be effected depends, in fact, chiefly on this difference.

When, however, we have to deal with a mixture of three substances, the difficulty is greatly enhanced, and if the boiling-points are not far apart it may be almost, if not quite impossible to separate any quantity of the middle substance in a state of purity by the ordinary methods of fractional distillation.

The variation in the composition of the distillate from a mixture of two substances, the boiling-point of which rises constantly during the distillation, has been carefully investigated by F. D. Brown (Trans. Chem. Soc. 1879, p. 550; 1880, pp. 49 & 304; 1881, p. 517)[*]; and his results may be briefly stated as follows:—Calling the relative weights of the two liquids at any instant in the still W_1 and W_2, the relative weights at the same moment in the vapour (and therefore in the distillate at this instant coming over from the mixture $W_1 + W_2$) x_1 and x_2, and the vapour-pressures of the pure substances at the boiling-point of the mixture, P_1 and P_2, the composition of the instantaneous distillate is given approximately by the equation

$$\frac{x_1}{x_2} = \frac{W_1}{W_2} \cdot \frac{P_1}{P_2},$$

but by substituting a constant, c, for the ratio $\frac{P_1}{P_2}$, thus

$$\frac{x_1}{x_2} = c \cdot \frac{W_1}{W_2},$$

a still better result is obtained.

[*] For an account of the experimental work and of the theoretical conclusions relating to the distillation of pairs of liquid that are (*a*) non-miscible, (*b*) miscible within limits, (*c*) miscible in all proportions, the article by one of us on "Distillation" in Thorpe's 'Dictionary of Applied Chemistry' may be consulted. Pairs of liquids belonging to the first and second classes boil at a lower temperature than even the more volatile component when distilled alone, and no separation can be effected by fractional distillation. Among those in the third class there are some from which only one of the two substances can be so separated; in each case of this kind there is a particular mixture (the composition of which varies to some extent with the pressure) which distils at a constant temperature without change of composition, and it is this mixture that would be separated by fractional distillation from that one of the pure substances which is present in excess. In some cases—such as propyl alcohol and water—the mixture of constant boiling-point and composition boils at a lower temperature than either of the liquids when distilled alone; in other cases—for example, formic acid and water—this mixture has a higher boiling-point than either component.

It is only when the boiling-point of every possible mixture lies between those of the components that both liquids can be separated by fractional distillation; it is only to such cases that Brown's law is applicable, and, in the case of three liquids, it is only such mixtures that are considered in this paper.

The ratio $\dfrac{P_1}{P_2}$ would, of course, vary to some extent during the distillation ; the value of the constant, c, does not differ greatly from the mean value of the ratio $\dfrac{P_1}{P_2}$.

This equation of Brown's may be written in the form

$$\frac{d\xi}{d\eta} = c\,\frac{\xi}{\eta},$$

where ξ = residue of liquid A at any instant,

  ,, $\eta =$,,   B   ,,

Taking L and M as the weights of A and B originally present, and $L+M=1$, we obtain by integration

$$\frac{M}{L}y\{c+(1-c)y\}^{c-1} = c^{c}(1-x)^{c-1}(1-y)^{c},$$

where y = quantity of the more volatile liquid A in unit weight of the distillate coming over at the instant when x is the quantity of liquid distilled.

By means of this equation we may trace the changes of composition that take place in the course of a distillation, and the variation in the composition of the distillate may be represented graphically.

To take a very simple case, let us suppose that $c=2$, and that $L=M=\frac{1}{2}$.

Fig. 1.
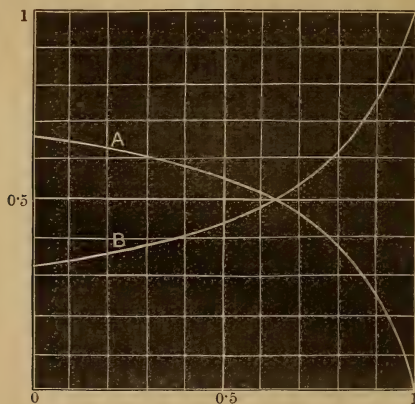
In the diagram (fig. 1) the amounts of distillate that have

been collected are represented as abscissæ, and the relative quantities of the two liquids A and B in the distillate at any moment as ordinates.

It will be seen that the composition of the distillate alters slowly at first, then more and more rapidly, also that while the first portion of the distillate contains a considerable amount of the less volatile substance B, the last portion is very nearly free from the lower-boiling component A. These points are fully confirmed by experiment.

By fractionating a few times in the ordinary way, collecting the distillates in six or eight fractions, we shall have a very large excess of A in the first fraction, and of B in the last.

Suppose now that we have two of these fractions, one containing A and B in the ratio of 9 : 1, and the other in the

Fig. 2.
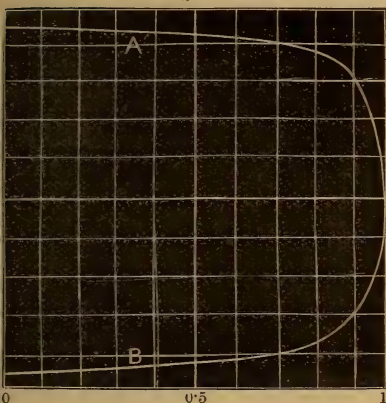
Fig. 3.
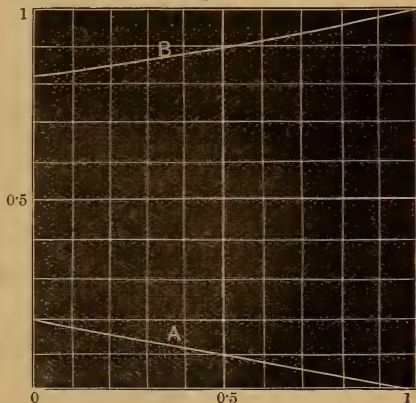
ratio of 1 : 9, and that we distil these fractions separately and completely ; the results will then be represented by figs. 2 and 3.

In making use of this formula it is assumed that no condensation (and therefore no fractionation) goes on in the still-head, but that the vapour reaches the condenser in the same state as when first evolved from the liquid in the still. It is obvious that by using a long still-head or a dephlegmator a more rapid separation would be effected.

In any case it is evident that after a sufficient number of fractionations, the first portion of the distillate from the first

fraction will be free from B, while the residue from the last fraction will be free from A.

Suppose now that our mixture contains a third substance, C, the boiling-point of which is higher than that of B.

It may be conjectured that in the progress of the distillation, the composition of the distillate at any instant will be analogous to that determined experimentally by Brown in the case of two liquids : namely, "the proportion of the three substances in the vapour forming the instantaneous distillate is the same as that of the weights of the three substances in the residue in the still, each weight being multiplied by a suitable constant which is roughly proportional to the vapour-pressure of the corresponding liquid."

With this assumption it is easy, as in the case of two liquids, to calculate curves representing graphically the progress of the distillation.

Let ξ, η, ζ = weights of the three liquids in the still at any instant ;

$\therefore d\xi, d\eta, d\zeta$ = weights of the three substances in the instantaneous distillate.

By hypothesis,

$$\frac{d\xi}{a\xi} = \frac{d\eta}{b\eta} = \frac{d\zeta}{c\zeta}.$$

Integrate

$$\frac{1}{a} \log \xi = \frac{1}{b} \log \eta + k = \frac{1}{c} \log \zeta + k'.$$

Let L, M, N be the original weights of the three liquids, and $(L + M + N = 1)$;

$$\therefore \frac{1}{a} \log L = \frac{1}{b} \log M + k = \frac{1}{c} \log N + k'.$$

Subtract

$$\frac{1}{a} \log \frac{\xi}{L} = \frac{1}{b} \log \frac{\eta}{M} = \frac{1}{c} \log \frac{\zeta}{N} ;$$

$$\therefore \left(\frac{\xi}{L}\right)^{\frac{1}{a}} = \left(\frac{\eta}{M}\right)^{\frac{1}{b}} = \left(\frac{\zeta}{N}\right)^{\frac{1}{c}}.$$

Let

y_1 = weight of A ⎫ in unit weight of distillate
y_2 =   „   B ⎬ coming over when x = weight
y_3 =   „   C ⎭ of liquid distilled ;

$$\therefore \quad y_1 = \frac{d\xi}{d\xi + d\eta + d\zeta} = \frac{a\xi}{a\xi + b\eta + c\zeta} \; ;$$

$$y_2 = \frac{b\eta}{a\xi + b\eta + c\zeta} \; ; \quad y_3 = \frac{c\zeta}{a\xi + b\eta + c\zeta}$$

Let

$$\frac{\xi}{\mathrm{N}} = z, \quad \frac{a}{c} = \lambda + 1, \quad \frac{b}{c} = \mu + 1 \; ;$$

$$\therefore \quad \xi = \mathrm{L}z^{\lambda+1}, \quad \eta = \mathrm{M}z^{\mu+1}, \quad \zeta = \mathrm{N}z \; ;$$

$$\therefore \quad 1 - x = \xi + \eta + \zeta = \mathrm{L}z^{\lambda+1} + \mathrm{M}z^{\mu+1} + \mathrm{N}z \; ;$$

$$y_1 = \frac{a\mathrm{L}z^\lambda}{a\mathrm{L}z^\lambda + b\mathrm{M}z^\mu + c\mathrm{N}} \; ; \quad y_2 = \frac{b\mathrm{M}z^\mu}{a\mathrm{L}z^\lambda + b\mathrm{M}z^\mu + c\mathrm{N}} \; ;$$

$$y_3 = \frac{c\mathrm{N}}{a\mathrm{L}z^\lambda + b\mathrm{M}z^\mu + c\mathrm{N}} .$$

The elimination of z from the expressions for x and y is impracticable, but the curves may be readily traced by treating z as an independent variable.

In the following curves (figs. 4 & 5) we have taken

$$a = 4, \quad b = 2, \quad c = 1, \quad [\text{and} \; \therefore \; \lambda = 3, \; \mu = 1],$$

these being nearly proportional to the vapour-pressures of methyl, ethyl, and propyl acetates.

I. represents the first distillation; in it $\mathrm{L} = \mathrm{M} = \mathrm{N} = \frac{1}{3}$. II. α, II. β, II. γ, II. δ, II. ϵ represent what would take place if the five fractions into which I. is divided were separately distilled; the composition of these fractions being found from the curves I. to be :—

	A or L.	B or M.	C or N.
II. α	·543	·300	·157
II. β	·47	·33	·20
II. γ	·37	·365	·265
II. δ	·22	·39	·39
II. ϵ	·047	·265	·687

Fig. 4.
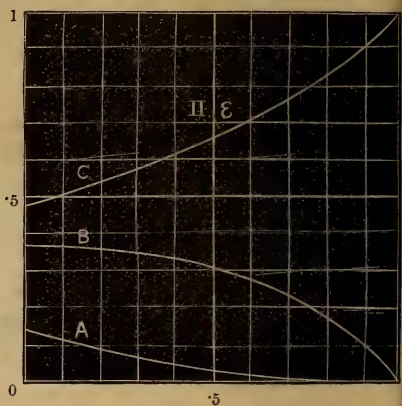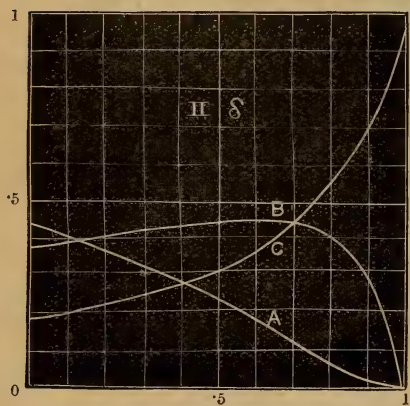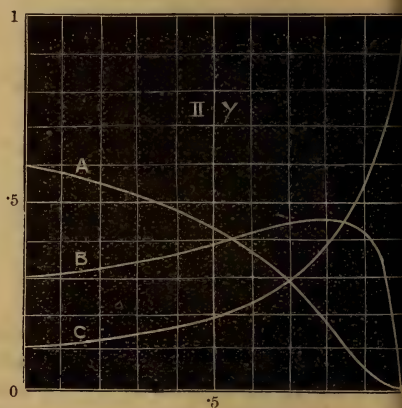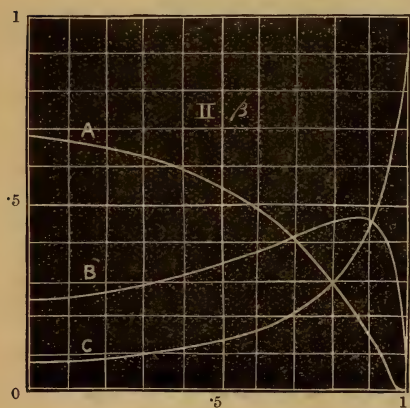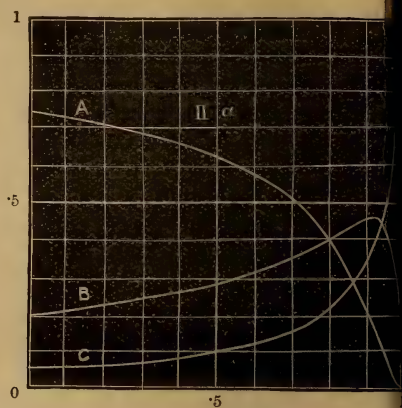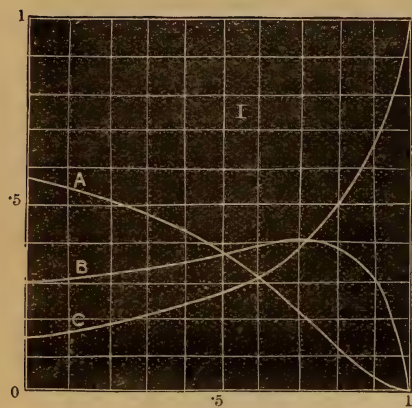
It is to be noted that in II. *α*, which is richest in the low-boiling liquid A, the amount of A rises from ·543 to an initial value ·74, and in the first half (or at least ⅖) of the distillate the aggregate amount of A rises to ·7.

In II. *ε*, which is richest in the high-boiling liquid C, the amount of C rises from ·687 to about ·9 in the last fifth, or ·82 in the last two-fifths of the distillate ; whereas in II. δ,

Fig. 5.
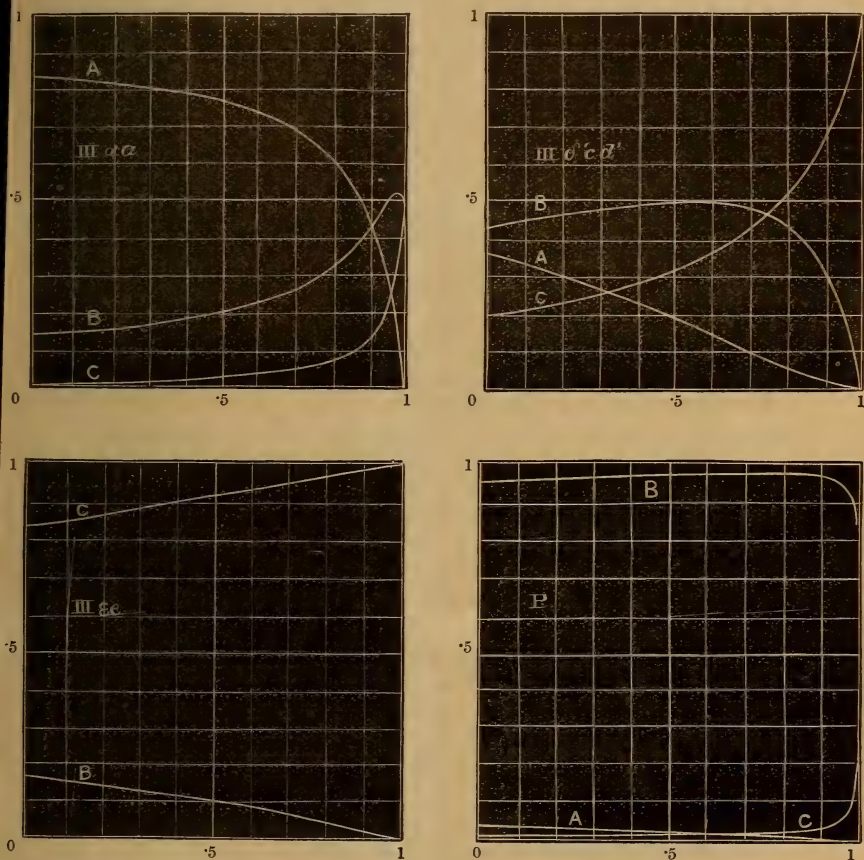
which is richest in B, the middle liquid, the amount of B rises merely from ·39, its initial value, to about ·45, its value for the fifth which is collected just after the first half (·5 to ·7). It is curious that in each of these distillations B rises to

practically the same maximum value, viz. ·45, the effect of the varying richness of the fractions in regard to B being merely to widen out or contract the B curve.

III. α *a*, III. δ " *c d*," III. ε *e* represent the distillation of those fractions of II. which are richest in A, B, and C respectively, and give some indication of the processes going on at the important stages of the third fractionation. In these A rises from ·7 to ·82, B from ·45 to ·5, C from ·9 to ·98. Here we notice that, owing to the small amount of C present in III. α*a* (whose original composition is A ·696, B ·239, and C ·065), B attains a higher maximum (·525) than it does (·496) in III. δ *cd*, which is far richer in B originally [A ·182, B ·44, C ·378].

P represents a distillation at an advanced stage of the fractionations—of a fraction rich in B. Its initial composition is A ·02, B ·96, C ·02. B is only advanced from ·96 to ·97 at the most favourable part of the curve, and is nowhere very free from C ; this points to the difficulty of obtaining B in a pure state by the ordinary method of fractionation.

The calculations for III. δ *cd* are appended as a specimen of the system employed (see table opposite): with the aid of the slide-rule they are very quickly effected.

Apart from the consideration of the above hypothesis and formulæ, it is clear that after five or six fractional distillations, carried out in the ordinary manner (but with a larger number of fractions than when only two substances are present), the first fraction will contain a large excess of A, a little of B, but very little, if any, of C ; the middle fraction will contain an excess of B with moderate quantities of both A and C ; the last fraction will consist almost entirely of C, the quantity of A, if present at all, being much smaller than that of B.

Now let us suppose that these fractions are distilled separately and completely. The first portion of the distillate from the first fraction will consist of A in a nearly pure state, and, even if it contains a little of B, will be free from C. Of the middle fraction the middle portion (or probably a rather later one) will be purest, but will contain a little of both A and C. The purest part of the last fraction will be the last portion (the residue in the still) and will be quite free from A though it may contain a little of B.

By proceeding with the fractionation in the usual manner we could obtain A and C in a pure state by separating each time the first small portion of the first distillate and the residue from the last distillate ; but we should have to carry the fractionation a very great deal farther before we could obtain B in a state of purity. We should, in fact, have to

$$L = ·182.$$
$$M = ·44.$$
$$N = ·378.$$

$$1 - x = ·182 z^4 + ·44 z^2 + ·378 z ;$$

$$y_3 = \frac{378}{378 + 880 z + 728 z^3}$$

z.	$·378 z$.	$·44 z^2$.	$·182 z^4$.	$1 - x$.	$880 z$.	$728 z^3$.	Denominator.	y_3.	y_2.	y_1.
0	0	0	0	0	0	0	378	1	0	0
·1	·038	·004	·000	·042	88	1	467	·810	·188	·002
·2	·075	·018	·000	·093	176	6	560	·675	·314	·011
·3	·114	·040	·001	·155	264	20	662	·571	·399	·030
·4	·151	·070	·005	·226	352	46	776	·488	·453	·059
·5	·189	·110	·011	·310	440	91	909	·416	·484	·100
·6	·227	·158	·024	·409	528	157	1063	·356	·496	·148
·7	·265	·216	·044	·525	616	249	1243	·304	·495	·200
·8	·303	·282	·074	·659	704	373	1455	·260	·483	·256
·9	·340	·356	·119	·815	792	530	1700	·222	·466	·312
1·0	·378	·440	·182	1·000	880	728	1986	·190	·443	·367

reduce the quantitities of A and C in this fraction until they both disappeared from the middle portion of the distillate, and an idea of the difficulty of attaining such a result may be gathered from the diagram P.

With substances whose boiling-points are not very far apart the rise of temperature during such a distillation would be almost imperceptible, and in the fractionation it would be necessary to collect a large number of fractions above and below the true boiling-point of B with very small temperature-ranges.   It would be necessary also to read the temperature with extreme care, and to make very accurate corrections for changes of the barometer (which would be impossible unless the vapour-pressures of the substance had previously been determined).

It has been pointed out, however, that after the mixture has been fractionated a few times, the first portion of the first distillate is free from C, while the residue from the last distillate is free from A.   If, therefore, after the fifth or sixth fractionation we remove these first and last portions each time, we shall gradually accumulate two quantities of liquid, one (the first portions) containing only A and B, the other (the residues) only B and C, and these may be separately fractionated in the ordinary way.

It is to be noticed also that as a quantity of liquid is removed each time, the total amount to be distilled, and therefore the time required for the distillation, gradually diminishes.

In arranging the fractions—as regards temperature—it is advisable, if the true boiling-points of the liquids are known, to take these temperatures and also the middle temperatures between the boiling-points of A and B and of B and C as definite points, and to arrange the fractions as far as possible symmetrically about these points.   There will thus be fractions of small and diminishing temperature-range above and below the boiling-point of B—and at the boiling-points of A and C after a few fractionations and until these substances are to a large extent eliminated—and fractions of large and increasing temperature-range above and below the two middle temperatures.

As the preliminary fractionation proceeds, more and more of A and C will be eliminated, so that after a time the boiling-point of the first portion of the lowest fraction will gradually rise, while that of the residue from the last fraction will gradually fall until either A or C disappear, or, if we proceed still further, until we have nothing but B left.   Much time

may therefore be saved if, instead of adding all the first portions of the lowest fractions together (and the same remark applies to the residues from the last fractions), we collect them in six or more different quantities. The final fractionations will then be in a forward state when the preliminary one is completed.

We shall in this manner obtain two quantities of B, one by the final fractionation of the first portions of the distillates from the lowest fractions of the preliminary fractionations, the other by that of the residues from the preliminary fractionations, and we can test the purity of the substance by comparing the boiling-points and the specific gravities of the two samples so obtained.

In order to test the value of this method, a mixture of 200 cub. cent. of methyl acetate (B.P. 57·1), 250 cub. cent. of ethyl acetate (B.P. 77·15), and 200 cub. cent. of propyl acetate * (B.P. 101·55) was distilled from a flask provided with a still-head one metre in length. The distillate was collected in four approximately equal fractions, numbered 5, 8, 11, and 14 under F in the table (I.) below. The observed temperatures (reduced to 760 millim.), the range of temperature for each fraction (Δt), the weight of each fraction (Δw), and the ratio of the weight to the temperature-range $\left(\dfrac{\Delta w}{\Delta t}\right)$ are also given in the tables. The second fractionation (II.) was carried out in the following manner:—the first fraction from I. (No. 5, B. P. 63°·8 to 71°·3) was distilled and the distillate collected in a separate receiver (No. 4) until the temperature rose to 63°·8 †, when receiver No. 5 was substituted for it and the distillation continued until the temperature rose to 71°·0. The gas was then turned out, and the second fraction from I. (No. 8, B. P. 71°·3 to 77°·8) added to the residue in the flask. Heat was again applied and the

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* The esters had previously been purified with great care, and were distilled separately from phosphorus pentoxide immediately before being mixed. Special precautions were also taken to avoid absorption of moisture during the fractionations. The methods of preparation and purification and proofs of the purity of the esters are fully described in the Trans. Chem. Soc. lxiii. p. 1194.

† The actual temperature was 63°·5, the barometric pressure being 751·1 millim.; the value of $\dfrac{dp}{dt}$ at the boiling-point is 27 millim. per degree for methyl acetate, 25 millim. for ethyl acetate, and 23 millim. for propyl acetate. All the temperatures are corrected to 760 millim. by means of these constants.

I.

F.	t corr. to 760 mm.	Δt.	Δw.	Δw/Δt
5.	63°.8–71°.3	7°.5	141.4	18.9
8.	71.3–77.8	6.5	145.2	22.3
11.	77.8–89.2	11.4	146.9	12.8
14.	above 89.2	......	143.3	
			576.8	

II.

F.	t corr. to 760 mm.	Δt.	Δw.	Δw/Δt
4.	60°.9– 63°.8	2°.9	59.7	20.6
5.	63.8– 71.0	7.2	134.2	18.6
8.	71.0– 77.1	6.1	98.4	16.1
11.	77.1– 84.4	7.3	67.2	9.2
13.	84.4– 91.7	7.3	51.0	7.0
14.	91.7– 98.4	6.7	86.1	12.7
15.	98.4–101.5	3.1	63.7	20.6
17.	above 101.5	......	14.3	
			574.6	

III.

F.	t corr. to 760 mm.	Δt.	Δw.	Δw/Δt
3.	58°.4 – 60°.95	2°.55	36.5	14.3
4.	60.95– 63.85	2.9	77.2	26.6
5.	63.85– 71.0	7.15	100.6	14.0
8.	71.0 – 77.15	6.15	75.4	12.4
11.	77.15– 84.4	7.25	67.7	9.3
13.	84.4 – 91.65	7.25	59.6	8.2
14.	91.65– 98.4	6.75	46.7	6.9
15.	98.4 –101.45	3.05	78.3	26.1
17.	101.45–101.55	0.1	19.7	197.0
Z ...	....	......	10.0	
			571.7	

IV.

F.	t corr. to 760 mm.	Δt.	Δw.	Δw/Δt
2.	57°.7 – 58°.6	0°.9	17.2	19.1
3.	58.6 – 61.0	2.4	58.1	23.7
4.	61.0 – 63.9	2.9	53.1	18.3
5.	63.9 – 71.05	7.15	85.1	11.8
8.	71.05– 77.15	6.1	66.6	10.9
11.	77.15– 84.3	7.15	84.7	11.8
13.	84.3 – 91.6	7.3	40.8	5.6
14.	91.6 – 98.4	6.8	33.8	5.0
15.	98.4 –100.95	2.5	44.1	17.6
16.	100.95–101.45	0.5	38.7	77.4
17.	101.45–101.55	0.1	24.2	242.0
Z ...	....	......	20.2	
			566.6	

V.

F.	t corr. to 760 mm.	Δt.	Δw.	Δw/Δt
2.	57°.1 – 58°.2	1°.1	19.4	17.6
3.	58.2 – 60.7	2.5	69.9	28.0
4.	60.7 – 63.85	3.15	49.0	15.3
5.	63.85– 71.0	7.15	69.0	9.6
8.	71.0 – 77.15	6.15	71.1	11.6
11.	77.15– 83.35	6.2	85.1	13.6
13.	83.35– 90.75	7.4	33.7	4.6
14.	90.75– 98.45	7.7	33.5	4.4
15.	98.45–100.95	2.5	29.4	11.8
16.	100.95–101.45	0.5	36.7	73.4
17.	101.45–101.55	0.1	31.1	311.0
Z ...	....	......	34.7	
			562.6	

VI.

F.	t corr. to 760 mm.	Δt.	Δw.	Δw/Δt
1.	57°.0 – 57°.3	0°.3	6.3	21.0
2.	57.3 – 58.2	0.9	28.5	31.7
3.	58.2 – 60.1	1.9	55.0	29.0
4.	60.1 – 63.85	3.75	54.2	14.3
5.	63.85– 70.75	6.9	47.4	6.9
7.	70.75– 75.7	4.95	52.0	10.4
8.	75.7 – 77.15	1.45	33.4	22.3
11.	77.15– 78.4	1.25	34.8	29.0
12.	78.4 – 82.5	4.1	47.9	11.7
13.	82.5 – 90.2	7.7	28.1	3.6
14.	90.2 – 98.45	8.25	27.8	3.3
15.	98.45–100.95	2.5	25.6	10.2
16.	100.95–101.45	0.5	30.3	60.6
17.	101.45–101.55	0.1	34.0	340.0
Z ...	....	......	50.6	
			555.9	

VII.

F.	t corr. to 760 mm.	Δt.	Δw.	$\frac{\Delta w}{\Delta t}$.
1.	57·05– 57·25	0·2	13·3	66·5
2.	57·25– 58·15	0·9	42·9	47·7
3.	58·15– 60·0	1·85	47·5	25·0
4.	60·0 – 63·8	3·8	43·5	11·4
5.	63·8 – 70·75	6·95	45·9	6·7
7.	70·75– 75·8	5·05	42·7	8·4
8.	75·8 – 77·2	1·4	45·0	32·1
11.	77·2 – 78·3	1·1	37·8	34·4
12.	78·3 – 82·1	3·8	41·1	10·8
13.	82·1 – 90·15	8·05	23·4	2·9
14.	90·15– 98·45	8·3	22·3	2·7
15.	98·45–100·95	2·5	17·6	7·0
16.	100·95–101 45	0·5	24·3	48·6
17.	101·45–101·55	0·1	23·7	237·0
Z ...	....	......	80·2	
			551·2	

VIII.

F.	t corr. to 760 mm.	Δt.	Δw.	$\frac{\Delta w}{\Delta t}$.
A ...	....	......	6·0	
1.	57·15– 57·35	0·2	11·7	58·5
2.	57·35– 58·25	0·9	49·1	51·6
3.	58·25– 60·15	1·9	45·4	23·9
4.	60·15– 63·8	3·65	36·0	9 5
5.	63·8 – 70·7	6·9	37·8	5·5
7.	70·7 – 75·8	5·1	41 9	8·2
8.	75·8 – 77·15	1·35	43·8	32·4
11.	77·15– 78·2	1·05	51·1	48·7
12.	78·2 – 81·1	2·9	34·1	11·8
13.	81·1 – 90·05	8·95	22·8	2·5
14.	90·05– 98·5	8·45	17·8	2·1
15.	98·5 –101·0	2·5	16·7	6·7
16.	101·0 –101·45	0·45	19·4	43·3
17.	101·45–101·55	0·1	12·6	126·0
Z ...	....	......	101·5	
			547·7	

IX.

F.	t corr. to 760 mm.	Δt.	Δw.	$\frac{\Delta w}{\Delta t}$.
A ...	....	......	11·4	
1.	57·0 – 57·25	0·25	18·6	74·4
2.	57·25– 58·0	0·75	44·5	59·3
3.	58·0 – 59·75	1·75	41·4	23·0
4.	59·75– 63·75	4·0	35·1	8·8
5.	63·75– 71·0	7·25	30·4	4·2
7.	71·0 – 75·95	4·95	39·9	8·0
8.	75·95– 77·15	1·2	47·9	39·9
11.	77·15– 78·05	0·9	57·9	64·3
12.	78·05– 80·55	2·5	27·1	10·8
13.	80·55– 89 9	9·35	20·4	2·2
14.	89·9 – 98·85	8·95	14·1	1·6
15.	98·85–101·05	2·2	12·8	5·8
16.	101·05–101·45	0·4	9·8	24·5
17.	101·45–101·55	0·1	6·3	63·0
Z ...	....	......	124·6	
			542·2	

X.

F.	t corr. to 760 mm.	Δt.	Δw.	$\frac{\Delta w}{\Delta t}$.
A ...	....	......	21·5	
1.	57·1 – 57·25	0·15	16·7	111·3
2.	57·25– 57·75	0·5	35·7	64·9
3.	57·75– 59·35	1·6	43·0	26·9
4.	59·35– 63·75	4·4	34·9	7·9
5.	63·75– 71·3	7·55	28·9	3·8
7.	71·3 – 76·1	4·8	36·9	7·7
8.	76·1 – 77·15	1·05	57·3	54·6
11.	77·15– 77·9	0·75	53·9	71·9
12.	77·9 – 79·9	2·0	23 3	11·7
13.	79·9 – 89·9	10·0	19·8	2·0
14.	89·9 – 99·3	9·4	12·5	1·3
15.	99·3 –101·1	1 8	9·7	5 4
16.	101·1 –101·5	0·4	8·4	21·0
17.	101·5 –101·55	0·05	3·5	70·0
Z ...	....	......	132·6	
			538·6	

XI.

F.	t. corr. to 760 mm.	Δt.	Δw.	Δw./Δt
A ...	....	......	31.5	
1.	57.1 – 57.2	0.1	15.2	152.0
2.	57.2 – 57.7	0.5	34.6	69.2
3.	57.7 – 59.1	1.4	36.4	26.0
4.	59.1 – 63.4	4.3	34.1	7.9
5.	63.4 – 71.5	8.1	23.9	3.0
7.	71.5 – 76.25	4.75	36.1	7.5
8.	76.25– 76.95	0.7	28.5	40.7
9.	76.95– 77.15	0.2	27.9	139.5
10.	77.15– 77.35	0.2	28.7	143.5
11.	77.35– 77.75	0.4	29.4	73.5
12.	77.75– 79.35	1.6	21.9	13.7
13.	79.35– 89.3	9.95	18.7	1.9
14.	89.3 – 99.55	10.25	10.9	1.1
15.	99.55–101.15	1.6	9.5	5.9
16.	101.15–101.45	0.3	6.0	20.0
Y ...	....	......	8.1	
Z ...	....	......	132.6	
			534.0	

XII.

F.	t corr. to 760 mm.	Δt.	Δw.	Δw./Δt
A ...	....	......	41.1	
1.	57.1 – 57.2	0.1	17.0	170.0
2.	57.2 – 57.65	0.45	30.5	67.8
3.	57.65– 58.9	1.25	30.3	24.2
4.	58.9 – 63.5	4.6	31.0	6.7
5.	63.5 – 71.9	8.4	23.8	2.8
7.	71.9 – 76.45	4.55	32.9	7.1
8.	76.45– 77.0	0.55	30.5	55.5
9.	77.0 – 77.15	0.15	27.6	184.0
10.	77.15– 77.3	0.15	36.2	241.3
11.	77.3 – 77.6	0.3	25.6	85.3
12.	77.6 – 78.85	1.25	18.7	14.9
13.	78.85– 88.9	10.05	17.9	1.8
14.	88.9 – 99.55	10.65	9.5	0.9
15.	99.55–101.15	1.6	8.1	5.1
X ...	....	......	7.8	
(Y & Z.)	....	......	140.7	
			529.2	

XIII.

F.	t. corr. to 760 mm.	Δt.	Δw.	Δw./Δt
A ...	....	......	50.4	
1.	57.1 – 57.2	0.1	20.4	204.0
2.	57.2 – 57.6	0.4	22.9	57.2
3.	57.6 – 58.7	1.1	26.0	23.6
4.	58.7 – 63.8	5.1	30.8	6.0
5.	63.8 – 72.35	8.55	21.3	2.5
7.	72.35– 76.65	4.3	35.2	8.2
8.	76.65– 77.05	0.4	23.2	58.0
9.	77.05– 77.15	0.1	33.1	331.0
10.	77.15– 77.25	0.1	38.0	380.0
11.	77.25– 77.5	0.25	21.5	86.0
12.	77.5 – 78.5	1.0	17.6	17.6
13.	78.5 – 88.7	10.2	18.7	1.8
14.	88.7 – 99.7	11.0	9.3	0.8
W ...	....	......	8.1	
(X to Z.)	....	......	148.5	
			525.0	

XIV.

F.	t corr. to 760 mm.	Δt.	Δw.	Δw./Δt
A ...	....	......	60.7	
1.	57.1 –57.2	0.1	14.7	147.0
2.	57.2 –57.6	0.4	23.6	59.0
3.	57.6 –58.6	1.0	22.6	22.6
4.	58.6 –64.25	5.65	29.9	5.3
5.	64.25–72.8	8.55	18.8	2.2
7.	72.8 –76.65	3.85	28.8	7.5
8.	76.65–77.05	0.4	27.1	67.7
9.	77.05–77.15	0.1	35.2	352.0
10.	77.15–77.25	0.1	43.1	431.0
11.	77.25–77.45	0.2	15.6	78.0
12.	77.45–78.2	0.75	17.4	23.2
13.	78.2 –84.7	6.5	16.0	2.4
V ...	....	......	11.4	
(W to Z.)	....	......	156.6	
			521.5	

XV.

F.	t corr. to 760 mm.	Δt.	Δw.	$\frac{\Delta w}{\Delta t}$.
A ...	....	......	70·1	
1.	57·1 –57·2	0·1	16·3	163·0
2.	57·2 –57·6	0·4	21·0	52·5
3.	57·6 –58·6	1·0	17·1	17·1
4.	58·6 –64·8	6·2	27·1	4·4
5.	64·8 –73·4	8·6	17·4	2·0
7.	73·4 –76·7	3·3	27·8	8·4
8.	76·7 –77·05	0·35	21·7	62·0
9.	77·05–77·15	0·1	43·0	430·0
10.	77·15–77·2	0·05	40·4	808·0
11.	77·2 –77·4	0·2	21·2	106·0
12.	77·4 –78·0	0·6	12·5	20·8
13.	78·0 –79·6	1·6	9·7	6·1
V ...	....	......	15·8	
(W to Z.) }	....	... ..	156·6	
			517·7	

XVI.

F.	t corr. to 760 mm.	Δt.	Δw.	$\frac{\Delta w}{\Delta t}$.
A ...	....	......	79·9	
1.	57·1 –57·2	0·1	14·6	146·0
2.	57·2 –57·6	0·4	17·3	43·2
3.	57·6 –58·6	1·0	14·6	14·6
4.	58·6 –65·35	6·75	25·0	3·7
5.	65·35–73·9	8·55	15·6	1·8
7.	73·9 –76·8	2·8	26·6	9·2
8.	76·8 –77·1	0·3	26·7	89·0
9.	77·1 –77·15	0·05	39·0	780·0
10.	77·15–77·2	0·05	39·9	798·0
11.	77·2 –77·35	0·15	24·4	162·6
12.	77·35–77·9	0·55	11·6	21·1
U ...	....	......	6·6	
(V to Z.) }	....	......	172·4	
			514·2	

XVII.

A ...	....	......	86·7	
1.	57·1 –57·2	0·1	14·4	144·0
3.	57·2 –57·6	0·4	14·3	35·7
3.	57·6 –58·6	1·0	13·5	13·5
4.	58·6 –65·8	7·2	22·4	3·1
5.	65·8 –74·4	8·6	15·9	1·8
7.	74·4 –76·85	2·45	24·7	10·1
8.	76·85–77·1	0·25	19·0	76·0
9.	77·1 –77·15	0·05	38·3	766·0
10.	77·15–77·2	0·05	48·0	960·0
11.	77·2 –77·3	0·1	22·0	220·0
12.	77·3 –77·65	0·35	9·6	27·5
U ...	....	......	10·2	
(V to Z.) }	....	......	172·4	
			511·4	

XVIII.

A ...	....	......	94·1	
1.	57·1 –57·2	0·1	11·3	113·0
2.	57·2 –57·6	0·4	13·4	33·5
3.	57·6 –58·6	1·0	10·7	10·7
4.	58·6 –66·25	7·65	21·3	2·8
5.	66·25–74·85	8·7	15·0	1·7
7.	74·85–76·85	2·0	21·4	10·7
8.	76·85–77·1	0·25	20·5	82·0
9.	77·1 –77·15	0·05	41·2	814·0
10.	77·15–77·2	0·05	49·6	992·0
11.	77·2 –77·3	0·1	21·0	210·0
T ...	....	......	6·0	
(U to Z.) }	....	......	182·6	
			508·1	

XIX.

A ...	....	......	100·3	
1.	57·1 –57·2	0·1	9·5	95·0
2.	57·2 –57·6	0·4	11·7	29·2
3.	57·6 –58·6	1·0	9·0	9·0
4.	58·6 –66·75	8·15	19·0	2·3
5.	66·75–75·35	8·6	15·7	1·8
7.	75·35–76·85	1·5	18·4	12·3
8.	76·85–77·1	0·25	18·3	73·2
9.	77·1 –77·15	0·05	39·5	790·0
10.	77·15–77·2	0·05	57·6	1152·0
11.	77·2 –77·3	0·1	13·9	139·0
T ...	....	......	9·7	
(U to Z.) }	....	......	182·6	
			505·2	

XX.

A ...	....	......	105·5	
1.	57·1 –57·15	0·05	5·9	118·0
2.	57·15–57·55	0·4	10·7	26·7
3.	57·55–58·55	1·0	8·9	8·9
4.	58·55–67·25	8·7	17·6	2·0
5.	67·25–75·95	8·7	16·6	1·9
7.	75·95–76·95	1·0	16·0	16·0
8.	76·95–77·15	0·2	13·4	67·0
9.	77·15 }	0·05 {	45·0 }	1888·0
10.	to 77·2 }		49·4 }	
11.	77·2 –77·25	0·05	13·0	260·0
S ...	....	......	8·6	
(T to Z.) }	....	......	192·3	
			502·9	

XXI.

F.	t corr. to 760 mm.	Δt.	Δw.	Δw/Δt.
A ...	......	......	105.5	
B ...	−57.15	......	11.6	
2.	57.15−57.55	0.4	7.2	18.0
3.	57.55−58.55	1.0	7.0	7.0
4.	58.55−67.2	8.65	16.3	1.8
5.	67.2 −76.3	9.1	18.2	2.0
7.	76.3 −77.0	0.7	11.2	16.0
8.	77.0 −77.15	0.15	25.3	168.6
9.	77.15 { slight rise }	} 0.0	38.7	} very high
10.			35.5	
11.	77.15−77.2	0.05	14.8	296.0
S ...	....	......	16.8	
(T to Z.)	....	......	192.3	
			500.4	

XXII.

F.	t corr. to 760 mm.	Δt.	Δw.	Δw/Δt.
(A & B.)			117.1	
C ...	−57.55	......	10.1	
3.	57.55−58.55	1.0	6.0	6.0
4.	58.55−67.2	8.65	12.6	1.5
5.	67.2 −76.5	9.3	19.2	2.1
7.	76.5 −77.05	0.55	15.4	28.0
8.	77.05−77.15	0.1	21.5	215.0
9.	77.15 { very slight rise. }	0 {	24.0	} very high
10.			36.6	
11.	77.15	...	17.3	
R ...	....	......	9.1	
(S to Z.)	....	......	209.1	
			498.0	

XXIII.

F.	t corr. to 760 mm.	Δt.	Δw.	Δw/Δt.
(A to C.)	....	......	127.2	
D ...	−58.55	......	8.6	
4.	58.55−67.2	8.65	9.1	1.1
5.	67.2 −76.7	9.4	21.7	2.3
7.	76.7 −77.1	0.4	14.4	36.0
8.	77.1 −77.15	0.05	16.6	332.0
9.	77.15	} 0	33.1	} very high
10.			25.2	
11.	77.15		11.5	
R ...	....	......	19.7	
(S to Z.)	....	......	209.1	
			496.2	

XXIV.

F.	t corr. to 760 mm.	Δt.	Δw.	Δw/Δt.
(A to C.)	....	......	127.2	
D ...	−58.55	......	10.0	
4.	58.55−67.2	8.65	6.8	0.8
5.	67.2 −75.3	8.1	15.1	1.9
6.	75.3 −76.8	1.5	7.8	5.2
7.	76.8 −77.1	0.3	12.2	40.7
8.	77.1 −77.15	0.05	14.6	292.0
9.	77.15	} 0	31.9	} very high
10.			26.9	
Q ...	....	......	13.1	
(R to Z.)	....	......	228.8	
			494.4	

XXV.

F.	t corr. to 760 mm.	Δt.	Δw.	Δw/Δt.
(A to D.)	....	......	137.2	
E ...	−67.9	......	10.2	
5.	67.9 −75.5	7.6	9.3	1.3
6.	75.5 −76.85	1.35	9.0	6.7
7.	76.85−77.1	0.25	13.2	52.8
8.	77.1 −77.15	0.05	20.2	404.0
9.	77.15	} 0	21.6	} very high
10.			19.1	
Q ...	....	......	23.2	
(R to Z.)	....	......	228.8	
			492.3	

XXVI.

F.	t corr. to 760 mm.	Δt.	Δw.	Δw/Δt.
(A to D.)	....	......	137.2	
E ...	−68.9	......	11.9	
5.	68.9 −75.7	6.8	7.1	1.0
6.	75.7 −76.9	1.2	10.4	8.7
7.	76.9 −77.1	0.2	15.4	77.0
8.	77.1 −77.15	0.05	16.4	328.0
9.	77.15	0	19.2	} very high
10.			12.1	
Q ...	....	......	32.3	
(R to Z.)	....	......	228.8	
			490.8	

distillate collected in receiver No. 5 until the temperature again rose to 71°·0, when it was replaced by receiver No. 8, and the distillation was continued until the temperature rose to 77°·1. The third fraction from I. (No. 11, B. P. 77°·8 to 89°·2) was then added to the residue in the flask, and the distillate collected in No. 8 until the temperature again rose to 77°·1, when No. 11 was put in its place. When the temperature had risen to 84°·4 a new receiver, No. 13, was substituted for No. 11, and the distillation was continued until the thermometer registered 91°·7. The last fraction from I. (No. 14, B.P. above 89°·2) was then added to the residue in the flask and the distillate collected in No. 13 until the temperature rose again to 91°·7, after which fractions were collected in No. 14 from 91°·7 to 98°·4, and No. 15 from 98°·4 to 101°·5, when the distillation was stopped, and the residue poured into receiver No. 17.

The third fractionation (III.) was carried out in a similar manner, a new fraction No. 3 being collected at the beginning. As the temperature rose to 101°·55, the true B.P. of propyl acetate, before the end of the last distillation, the residue in the flask consisted of this substance in a nearly pure state, and it was therefore collected in a separate flask Z, and was not redistilled during the preliminary fractionations. The residues from the subsequent fractionations up to the tenth were collected in Z, but after this, as a large amount of propyl acetate had been removed, the temperature did not reach 101°·55, and the residue from the eleventh fractionation (B. P. above 101°·45) was collected in a new flask, Y.

At the end of the twelfth fractionation the temperature rose only to 101°·15, and the residue was therefore placed in a third flask, X, and subsequently the residues were collected in W, V, &c., to Q, as shown in the tables.

It was not until the fifth fractionation that the first fraction began to boil at 57°·1, the B.P. of methyl acetate, and it was not thought advisable to separate the first portion of the first distillate until the eighth fractionation. This portion and also the corresponding ones up to the twentieth fractionation were collected together in flask A, after which the first portions were collected in B, C, D, and E.

The ratios $\frac{\Delta w}{\Delta t}$ give an indication of the purity of the various distillates, for with a pure substance, since $\Delta t = 0$, $\frac{\Delta w}{\Delta t} = \infty$, while with a very impure substance there is a rapid

rise of temperature during distillation, and $\dfrac{\Delta w}{\Delta t}$ is consequently small.

It will be seen that the ratio for the highest fraction rises rapidly, being 197 in the third fractionation and rising to 340 in the sixth, after which it diminishes again owing to removal of propyl acetate in the residues. The value for the lowest fraction increases much more slowly, reaching a maximum of 204 in the thirteenth fractionation, and afterwards diminishing owing to removal of methyl acetate.

The presence of the middle substance, ethyl acetate, is not clearly shown until the fourth fractionation, when the value of $\dfrac{\Delta w}{\Delta t}$ for the sixth distillate (No. 9) is higher than for those above and below it; but the gradual accumulation of the ethyl acetate in the middle fractions in subsequent fractionations is clearly shown by the rise in the values of $\dfrac{\Delta w}{\Delta t}$ for fractions 8 and 11, and after the tenth fractionation in fractions 9 and 10. The range of temperature for fractions 9 and 10 was gradually diminished from $0°·2$ each in the eleventh fractionation until no rise could be detected; there was indeed no perceptible rise of temperature during the collection of No. 11 in the twenty-second and twenty-third fractionations. It was therefore certain that after the twenty-sixth fractionation the tenth fraction was free from propyl acetate, and that the remaining fractions Nos. 5 to 10 contained only methyl and ethyl acetates.

The preliminary series of fractionations was therefore completed, no fraction now containing more than two substances.

The progress of the separation is well seen by mapping the temperatures against the total weight of distillate collected. The curves I. to XII. represent the first twelve fractionations, the weight of distillate being given in each case as percentages. The dotted lines at the extremities of the later curves represent the methyl and propyl acetates removed in the first portions of the first distillates and in the residues.
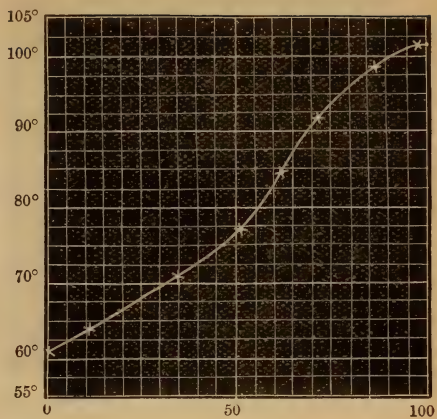
The presence of the middle substance is clearly indicated in the fourth curve, but not in the earlier ones.
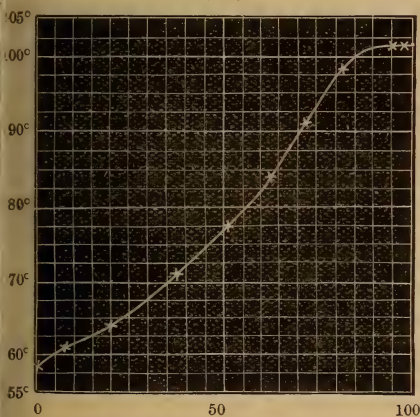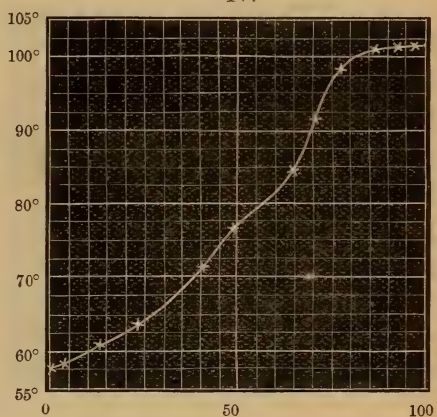
Fig. 6.
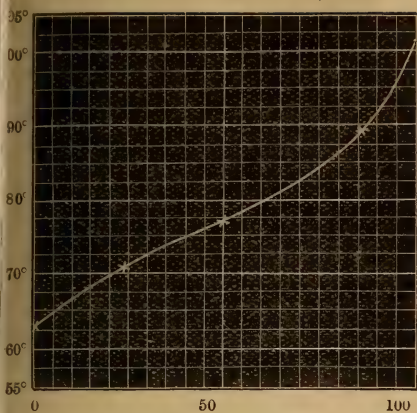
VII.
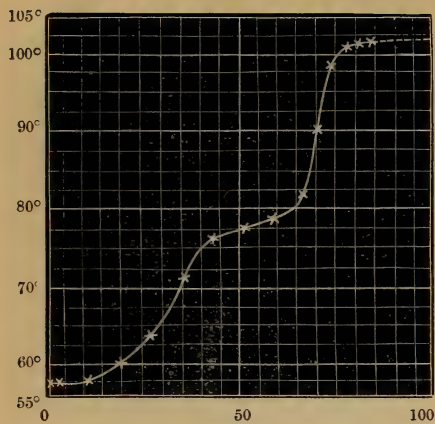
VIII.
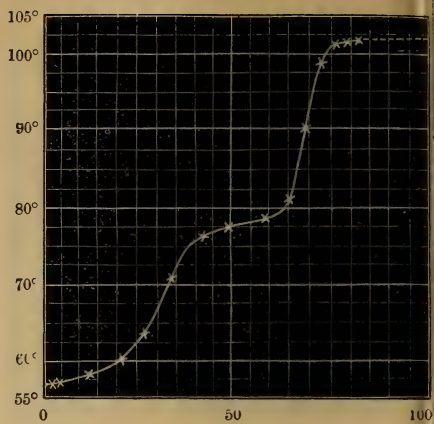
IX.

X.

XI.

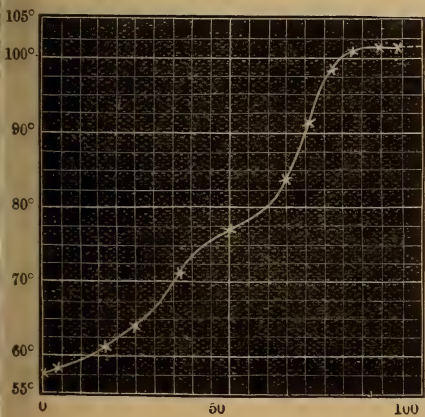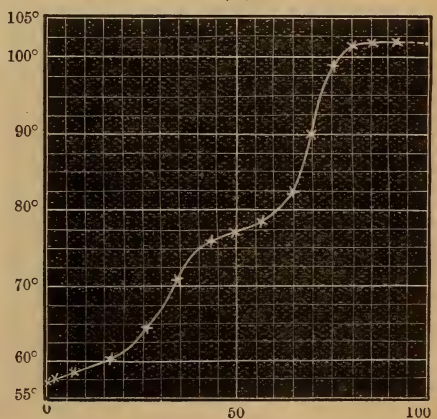XII.

Final Fractionations.

The fractions into which the esters had been separated at the end of the 26th preliminary fractionation are given below :—

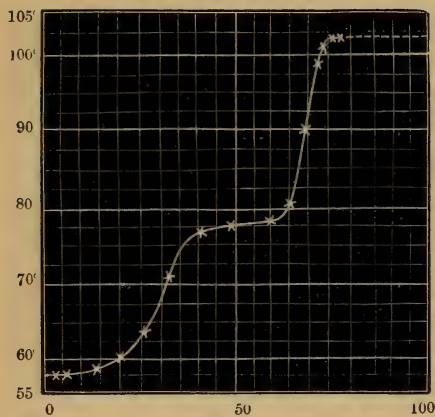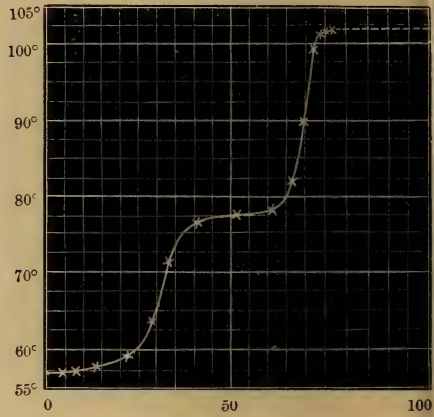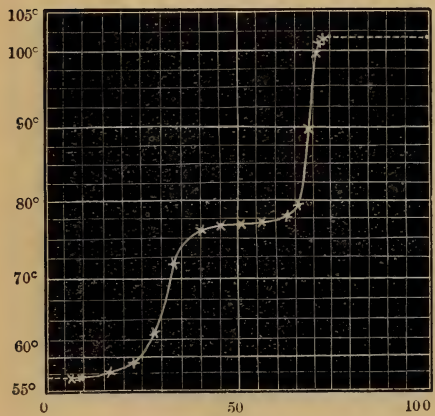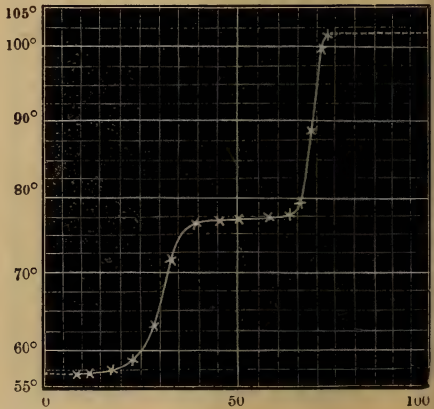| Methyl and Ethyl Acetates.			Ethyl and Propyl Acetates.		
Fraction.	Temperature range.	Weight.	Fraction.	Temperature range.	Weight.
A ...	57˚1	105·5	Q ...	77˚15	32·3
B ...	below 57·15	11·6	R ...	above 77·15	19·7
C ...	,, 57·55	10·1	S	,, 77·2	16·8
D ...	,, 58·55	10·0	T	,, 77·3	9·7
E ...	,, 68·9	11·9	U ...	,, 77·65	10·2
5 ...	68·9–75·7	7·1	V ...	,, 79·6	15·8
6 ...	75·7–76·9	10·4	W ...	,, 99·7	8·1
7 ...	76·9–77·1	15·4	X ...	,, 101·15	7·8
8 ...	77·1–77·15	16·4	Y ...	,, 101·45	8·1
9 ...	77·15	19·2	Z ...	,, 101·55	132·6
10 ...	77·15	12·1			
		229·7			261·1

The total weight was 490·8, so that 86 grams had been lost by evaporation and through adherence to the flasks and to the funnel through which the liquid was poured into the still.

The final separation of the esters was carried out in the following manner :—

Ethyl Acetate (1).—The fractions 5 to 10 consisted of ethyl acetate with some methyl acetate. The final fractionations in this case were a continuation of the preliminary ones and were carried out in the same manner. No. 10 was almost if not quite pure ethyl acetate, and was only distilled once more; the first portion was collected in No. 9, and the residue was taken as pure. In the remaining six fractionations the residue, after the distillation of No. 9, was each time taken as pure, and the total amount of ethyl acetate thus obtained was 56·1 grams.

Ethyl Acetate (2).—The flasks Q to U contained ethyl acetate with some propyl acetate. In the six fractionations, which were carried out in the usual way, the first portion of the distillate from Q was each time taken as pure, the small residue in the still being rejected. The weight of pure ethyl acetate obtained from this series was 62·7, and the total weight was therefore 118·8 grams, or about 53 per cent. of that originally taken.

Methyl Acetate.—The flasks A to E contained methyl acetate with some ethyl acetate. Although special care had been taken to prevent absorption of moisture, it was found that a

little water was present : in two fractionations, therefore, phosphorus pentoxide was placed in the distillation-bulb, which was heated by a water-bath. After the first fractionation the first portion of the distillate from the first fraction was taken as pure, the small residue in the still being each time rejected. There were altogether nine fractionations, and the amount of pure methyl acetate obtained was 88 grams, or about 48 per cent. of that taken. (The loss of this ester by evaporation would be greater than that of either of the other two.)

Propyl Acetate.—The flasks V to Z contained propyl acetate with some ethyl acetate. It was found that the first two residues were slightly acid, owing to hydrolysis of the esters by the trace of water present. These two residues were therefore collected separately and were shaken with a strong solution of potassium carbonate ; the ester was then washed with water, dried with phosphorus pentoxide, and again distilled. Five fractionations were found sufficient to purify the propyl acetate, the residues being each time taken as pure (except the first two, which were treated as described). The total weight of pure propyl acetate was 126·8 grams, or 72 per cent. of that taken. (The loss by evaporation would be smallest in this case.)

The esters were then distilled from phosphorus pentoxide, and their specific gravities at 0° determined by Sprengel's method as modified by Perkin. The completeness of the separation was proved by the close agreement of the results with those obtained before mixing, as well as by the identity of the boiling-points with those previously determined.

The specific gravities are given below :—

<div align="center">Specific Gravities at 0°.</div>

	Previous Determinations.	After Fractionation.
Methyl acetate * (a).........	·95929	·95937
,, ,, (b).........	·95934	
Ethyl acetate * (a)	·92434	(1) ·92438
,, ,, (b)	·92438	(2) ·92437
Propyl acetate * (a).........	·91017	·91008
,, ,, (b).........	·91015	

* Two different samples of each ester had been purified and their specific gravities determined. The two results are given in each case, in order to show what error of experiment might be expected. The two samples of each ester were afterwards mixed together.

Apart from the comparison of the specific gravity of the ethyl acetate before mixing and after fractionation, a proof of the purity of this substance is afforded by the agreement between the specific gravities of the two samples, since, if the separation had been incomplete, one would have been contaminated with methyl acetate, the other with propyl acetate.

III. *On Endothermic Decompositions obtained by Pressure.* (*Second Part.*) *Transformations of Energy by Shearing Stress.* *By* M. CAREY LEA[*].

OF the relations which exist between two forms of energy, mechanical and chemical, very little, if anything, is known. In the second volume of his *Lehrbuch* Ostwald remarks that as to these relations " almost nothing " is known[†].

There are certain familiar cases in which mechanical energy may seem at first sight to be converted into chemical energy. The fulminates, iodimide, and other substances explode by shock. But it is hardly necessary to remark that all such reactions are exothermic, and need an external impulse only to start them—if this impulse were not needed such compounds could not exist at all. Were such reactions taken as true transformations of energy, an absence of due relation between cause and effect would be involved ; for the shock that suffices to explode a grain of fulminate will equally explode a ton, and the faint spark that will explode a grain of gunpowder will also explode a magazine.

Present opinion holds undoubtedly that no true transformation of mechanical into chemical energy is known. Most text-books do not consider the question at all. But Dr. Horstmann, in the volume of theoretical chemistry which forms part of the last German edition of Graham-Otto's ' Chemistry,' discusses the matter. His views are so much to the point that I shall translate a few sentences, putting in italics the statements to which I would specially refer.

" We must consequently admit that through a rough mechanical attack the molecular structure of certain chemical compounds can be disrupted and destroyed. This will certainly be possible only for compounds in whose molecules the arrangement of the atoms does not correspond to a stable

[*] Communicated by the Author.
[†] " Anderseits ist von dem Verhältniss zwischen mechanischer und chemischer Energie fast nichts bekannt." A few lines below this remark is repeated with emphasis. *Lehrbuch*, 2nd German ed. vol. ii. p. 12.

equilibrium, and in which, therefore, the chemical energies themselves are already striving to form simpler and more stable compounds out of the constituents of the existing substance. *For it cannot be admitted that actual chemical changes can be brought about by a mechanical impulse* " (l. c. p. 350).

In another chapter he says with equal distinctness :—

" *By mechanical means alone no reaction against the force of chemical energy can be brought about.* By a shock or blow the molecular structure of chemical compounds can indeed be so far loosened that free play is given to chemical forces ; *but against these forces we cannot by mechanical means separate the atoms nor combine them in a definite way* " (p. 594).

These expressions of a distinguished chemist will sufficiently indicate what has been up to the present time the opinion of chemists as to the possibility of transforming mechanical energy into chemical.

In the first part of this paper I believe I have been able to show in a qualitative way the production of true endothermic reactions by mechanical force. In the present part I hope to show an increased number of such reactions, and in one case to exhibit actual quantitative results, at least so far as to obtain the product of the transformation in weighable quantities.

In the first part decompositions were described that were brought about by *simple pressure*. Compounds formed by exothermic reactions, and therefore requiring expenditure of energy to break them up, were decomposed. The investigation might probably have been made to include a still larger range of substances. But it was found that the efficiency of pressure was so enormously increased by the addition of shearing motion, that decompositions requiring a force of hundreds of thousands of pounds with pressure alone could be effected by the mere strength of the hand when shearing-stress was used. More than this, decompositions which enormous pressures failed to effect readily took place under the action of shearing-stress *.

* It would not have been difficult to obtain much greater pressures than those described in the first part of this paper. This could be effected by means of the differential screw. I had planned for a screw with threads of 40 turns in 10 inches and $39\frac{1}{3}$ turns in 10 inches respectively. The mechanical efficiency of such a screw is that of one having 320 turns to the inch, if such a thing were practicable, at the same time that a thoroughly strong construction can be obtained. The massive steel nut to advance $\frac{1}{8}$ of an inch would require 40 full turns of this screw.

This arrangement compares as follows with that previously employed. In it to cause the vise-jaws to approach by 1 inch required that the point of the lever at which the force was applied should pass through a space

I.

It was mentioned in a previous paper on the decomposition of the silver haloids by mechanical force that when silver chloride was sharply ground for some time in a mortar, both the pestle and mortar became covered with a deep purple varnish of silver photochloride, thus indicating a partial reduction to subchloride. It has since proved that there is no more effectual method than this of applying shearing-stress, and that in this way a number of quite stable chemical compounds formed by exothermic reactions can be broken up. The mortar and pestle should be very solid and of unglazed porcelain. With metal there would be danger of action between the metal and the substance, and with agate mortars sufficient force cannot well be applied. In many cases success depends on the exertion of great pressure on the pestle. It is also absolutely essential that the quantity of material acted upon should be small. When a larger quantity is employed the particles slip or roll over each other and thus escape the action of the stress. It is no doubt for this reason that the very remarkable results which can be obtained in this way have hitherto escaped attention.

A small quantity, a few decigrams, of the substance having been placed in the mortar, the first thing is to spread it in a thin uniform coat over the bottom and part of the sides. The pestle is then to be rotated with the utmost force that can be exerted.

Sodium Chloraurate.—The salts of gold are particularly well adapted to this examination, as the reduction is complete and the gold appears in the metallic state so that it can be weighed and the exact amount of reduction can be fixed. It

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of 113·1 feet: this relation, 1 inch to 113·1 feet or 1 : 1357·2, gives the measure of the efficiency of the instrument.

With the double screw, on the other hand, to cause the nut to advance $\frac{1}{8}$ of an inch, the end of the lever (2 feet long) must pass through a space of 500 feet, or in the proportion of 1 inch to over $\frac{3}{4}$ of a mile. The circumference described by the lever being approximately $12\frac{1}{2}$ feet, and the screw requiring 40 turns to advance the nut $\frac{1}{8}$ of an inch, we get the proportion of 1 inch to 4000 feet, or 1 to 48,000, which is the measure of the efficiency of such an instrument. Therefore, supposing two men to pull on the end of the lever each with a pull of 100 lb., the pressure exerted on the nut (disregarding loss by friction) would be 9,600,000 lb., which could be doubled by using a 4-foot lever.

Such a combination is quite practicable, the only real difficulty being to obtain sufficient solidity of construction to resist strain. I had made drawings for this instrument, but gave it up in consequence of observing the enormously greater efficiency of shearing-stress as a means of transforming mechanical into chemical energy.

will be seen by (3) below that it may amount to as much as over 4 per cent. of the gold present.

(1) Two or three decigrams of chloraurate with a moderate trituration left 1·8 milligram of metallic gold. Under the action of the pestle the yellow colour of the salt gradually deepened to an olive shade. When water was poured on, the undecomposed salt dissolved, leaving the gold as a delicate purple powder. The colour of the gold being purple instead of the more usual brown shade explains the olive colour just mentioned, yellow and purple combining to form olive.

(2) Half a gram of the salt was taken. This specimen was more neutral than the preceding, and was therefore more easily reduced. Half an hour's trituration had for effect the reduction of 9·2 milligrams of gold.

(3) A similar treatment of the same quantity of chloraurate resulted in the separation of 10·5 milligrams of gold.

These may seem at first somewhat small proportions. But it is to be recollected that the force is necessarily applied at a disadvantge, and that the equivalent in work of chemical affinity is always very large. In the present case the figures are as follows :—Thomsen found as the heat-equivalent for the combination of gold with chlorine to form auric chloride 28·8 great calories. Taking the atomic weight of gold as 197, we find that one gram of gold in forming auric chloride disengages 115·7 small calories or water-gram-degrees, whose equivalent, taking Rowland's determination, is 49,288·2 gram-metres, corresponding to $4·83 \times 10^9$ ergs or 483 joules.

The small quantity of gold reduced in (3), 10·5 milligrams, would by conversion to auric chloride generate 1·215 water-gram-degrees of heat whose equivalent in work is 518 gram-metres. As heat is a degraded form of energy, such an actual transformation without loss to a higher form would be impossible. It is more correct to say, therefore, that the amount of energy which would raise 518 grams to the height of one metre can be transformed into the same amount of heat, 1·215 water-gram-degrees, as is evolved by 10·5 milligrams of gold by conversion into auric chloride. Consequently this work, 518 gram-metres, represents the amount of mechanical energy transformed into chemical energy in operation (3) *.

It does not appear that in effecting these reactions and the

* The amount of energy required would, in fact, slightly exceed this, as the thermochemical equivalent of formation of sodium chloraurate would slightly exceed that of auric chloride. For this chloraurate I do not find a determination, but preferred to use this salt in the operation as being both more stable and more neutral than auric chloride.

others which remain to be described, mechanical energy undergoes an intermediate conversion into heat. Rapid movements are not needed ; what is required is strong pressure with movement, but this need not be rapid. Nor does the mortar or the pestle become sensibly warm. The operation does not need to be continuous, but may be broken up with any number of intervals. But a decisive conclusion can be drawn from those cases in which decompositions are effected in this way that *cannot be produced by heat*. For example, in the next instance to be mentioned there is a partial reduction of corrosive sublimate to calomel. By heat, corrosive sublimate sublimes unaltered, and the same is true of mercurous chloride. The three silver haloids fuse unchanged at a red heat. The same conclusion can be drawn from other reactions.

These results were obtained in an atmosphere absolutely free from dust, so that the reducing action of this substance was completely excluded.

Mercuric Chloride.—A specimen which, after lightly powdering, did not darken in the least with ammonia, was triturated in the manner just described with several intervals, in all for 15 minutes. It then became grey in a very striking way when moistened with ammonia.

This is a very interesting reaction. In the first part of this paper it was mentioned that mercuric chloride could be subjected to a pressure of about 70,000 atmospheres absolutely without change. It appears, however, that a pressure amounting to less than a hundred pounds causes decomposition when combined with movement, showing the enormously greater efficiency of shearing-stress as compared with simple pressure. Not only this but, as just mentioned, shearing-stress produces decompositions which heat is not competent to effect.

Mercurous Chloride.—When calomel was sharply triturated in a mortar, it first became yellow and then blackened without difficulty.

Turpeth Mineral, $3HgO,SO_3$.—Reduces rather slowly.

Mercuric Oxychloride, $2HgO, HgCl_2$, obtained by precipitating corrosive sublimate by potash acid carbonate, exhibited the following reaction. Its brownish-purple colour by light grinding became lighter, and then when strong force was used it blackened with remarkable ease.

Mercuric Iodide shows a trace of blackening.

Mercuric Oxide.—This substance yields much more readily to trituration than to simple pressure. Especially on the sides of the mortar it was quite blackened. The layer of material must be quite thin, otherwise little effect is produced,

Platinic Chloride.—Gradually darkened in a very marked way, finally becoming blackish.

Ammonium Platinichloride gave same result.

Silver Tartrate.—When spread in a very thin skin over the mortar, each sharp stroke of the pestle left a black line behind it. This is a strong contrast with the complete resistance of this substance to simple pressure.

Silver Carbonate.—Action similar.

Silver Citrate.—Blackens very easily.

Silver Oxalate.—At least as easily.

Silver Arsenate.—Nearly as easily.

Silver Sulphite.—Effect visible in five minutes and gradually increasing. Very well marked.

Silver Salicylate.—No other silver salt appears to be so easily reducible as this. Every sharp stroke of the pestle leaves a brown mark behind it.

Silver Orthophosphate.—Affected easily. After the phosphate has been a good deal reduced, the unchanged part may be dissolved out with ammonia. The black residue after washing readily dissolves in dilute nitric acid, and the solution gives a white cloud with hydrochloric acid.

Potassium Ferridcyanide.—A crystal of the pure salt sharply ground in a mortar becomes in portions brown and in others blue. The quantity used must, as indeed in all of the above cases, be small, one or two decigrams. If a little distilled water be added an insoluble blue powder is left behind, and the solution formed strikes a blue colour when added to one of ferric alum. This indicates that the decomposition is twofold. The experiment is quite a striking one, and the result is easily obtained.

II.

This form of mechanical force, shearing-stress, may be applied to effect endothermic change in other ways. A very simple, and at the same time very efficient, method is that of pressure with a glass rod. Pure strong paper is to be imbued with a solution of the substance, if it is soluble, or if not, it is to be made into a paste with water and then applied with a brush. This paper is to be then very thoroughly dried, and is to be laid upon a piece of plate glass. Characters are to be marked on it with the end of a glass rod that has been rounded by heat, using as much pressure as is possible without tearing the paper.

More than twenty years ago I was able to show that marks made in this way on sensitive photograph-films could be developed, as an invisible image had been impressed. That,

however, is a somewhat different matter from actual and visible decomposition following each stroke of the rod, a result which may be obtained with various salts of gold, mercury, silver, and other metals.

Potassium Ferridcyanide.—Pure paper was imbued with a dilute solution of this salt. After thorough drying it was laid on a glass plate, and marks were made with a glass rod in the manner just described. These marks were immediately visible, and when the paper was plunged into dilute solution of ferric ammonia alum or of ferric chloride they became dark blue. It is probable that the decomposition here effected was twofold (see above).—The *nitroprussides* appear to be much more stable than the ferridcyanides. When sodium nitro-prusside paper was treated with pressure followed by appropriate reagents, no indications of decomposition were obtained.

Auric Chloride.—Paper imbued with a solution of auric chloride and marked in the manner described was thoroughly soaked in water to remove, as far as possible, the rest of the gold salt. The marks were very distinct and gradually gained with time. Colour dark purplish grey.

Platinic Chloride.—After drying and marking, the paper was thoroughly soaked in water and dried. The marks were very distinct, of a yellow colour.

Ammonium Platinichloride.—Marks very visible. Continued to slowly deepen, and in a few weeks were almost black.

Silver Carbonate.—The traces of the rod were brown. When the paper was placed in ammonia the carbonate dissolved, but the marks resisted the action of the ammonia and remained.

Silver Phosphate.—Action very similar to the preceding.

Silver Arsenate.—Similar action.

Silver Tartrate and Oxalate.—These salts gave analogous results to the preceding, but not so well marked. The carbonate, phosphate, and arsenate show this reaction best, and about equally well. What is rather curious is that silver chloride does not exhibit a visible action.

Mercuric Oxide.—Paper imbued with a saturated solution of mercuric nitrate and then treated with solution of potash and dried shows this reaction very distinctly. Mercuric oxide appears to be quite sensitive to light.

Turpeth Mineral.—Mercuric sulphate was dissolved in water with the aid of sulphuric acid. Paper was soaked in the solution, allowed to become nearly dry, and then washed. This paper showed the reaction very moderately, but the marks were brought out more strongly by immersion in ammonia.

Ferric Alum (Ammonia).—Paper imbued with solution of this salt, dried and marked, was immersed in solution of potassium ferridcyanide. The marks came out blue, showing that the ferric salt had undergone partial reduction.

It is easily conceivable that the action of shearing-stress should be enormously greater than that of simple pressure. For it seems probable that pressure can only cause decomposition when the resulting product is more dense, has a greater specific mass, than the original substance. With shearing-stress the case is altogether different. All matter is in a state of vibration, and it is easily conceivable that the forcible friction of a hard substance may increase vibration in somewhat the same way as does a bow drawn over a stretched cord. Both the elasticity and the tension of the atoms themselves are vastly greater than those of any stretched cord, so that the increased vibration may easily be sufficient to shatter the molecule.

The transformation of light, heat, and electricity into mechanical energy, as well as the converse transformations, are extremely familiar. That mechanical energy may be transformed into chemical energy is proved by the results described in these papers. The converse transformation, that of chemism into work, is in an industrial point of view by far the greatest chemical problem now awaiting solution. But it is by no means certain that such a transformation is practically possible. At least it seems probable that the improvement in our method of obtaining work from the chemism of carbon may be in the direction of substituting electricity for heat as the intermediary.

IV. *On an Approximate Law of the Variation in the Pressure of Saturated Vapours. By the late* **K. D. Krae-vitch** [*].

THE dependence between the pressure of a vapour in a state of saturation and the temperature is probably expressed by an exceedingly complex function, which, notwithstanding the endeavours of many renowned physicists, has not yet been determined. Even the interpolation (empirical) formulæ, with the exception of Biot's formula, cannot be regarded as satisfactory. The cause of failure is to be found in the endeavour to attain the dependence sought for in all its exactitude, which is probably excessively difficult (if not impossible) to do, because the pressure of a vapour in a state

of saturation depends, not only on the temperature, but also on a number of other circumstances: on the properties of the liquid (coefficient of expansion, latent heat of vaporization, specific heat, &c.), and of the vapour (coefficient of expansion, specific heat, molecular weight, &c.). In the present stage of science it would be well to search for even an approximate dependence between vapour-pressure and other thermal quantities, and there is no necessity to limit this dependence to a function of temperature; and it might be deemed a considerable scientific success were an expression found for the pressure of a vapour in a state of saturation, in dependence upon any thermal quantity whatever. The finding of such a dependence is naturally easier than that of a precise function, and one, especially, of temperature only[*]. Such approximate inexact laws and formulæ would serve as guiding clues for further researches and for the discovery of more exact laws.

In this paper it is my object to show that the pressure of a vapour is in a somewhat simple, although only approximate, dependence upon other observable quantities; or, in other words, if certain quantities are known, corresponding to a definite temperature, having a special significance, then it is possible to calculate with sufficient accuracy the vapour-pressure for temperatures near to it, and approximately also for temperatures far removed.

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1. Let us imagine a kilogramme of a liquid at a temperature of vaporization t under a pressure p, and let us convert it by two methods into vapour saturating a space, at a temperature $t + dt$ and under a pressure $p + dp$, and calculate each time the increase of internal energy in the material.

(a) Let us increase the pressure p on the liquid by dp[†] and heat it to the new boiling-point $t + dt$, corresponding to the new pressure. The internal energy of the substance will then increase by cdt, where c is an amount of heat which is slightly less than the specific heat of the liquid. In the case of a small external pressure we can neglect this difference, because the coefficient of expansion and specific volume of the liquid, upon which the amount of heat consumed in external work depends, are exceedingly small. This difference only becomes significant

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[*] I have written more fully on the importance of researches of this kind in my papers, "Remarks on Van der Waals' Formula" (Journal of the Russian Physico-Chemical Society, vol. xix.), "On the Dependence of the Latent Heat of Vaporization upon other Factors" (Idem, xxi.), and in the *Repertorium der Physik* (vol. xxvi. p. 589).

[†] The internal energy of a liquid then decreases, but so slightly that we do not take it into consideration.

for abnormally high pressures, or when the coefficient of expansion of the liquid becomes great. On the liquid attaining the temperature $t + dt$ under the pressure $p + dp$, let us convert it into saturated vapour at the same temperature and pressure. If ρ denote the internal (potential) latent heat of vaporization for the temperature t, we find that the internal energy of the liquid increases by $\rho + d\rho$ on its conversion into vapour at a temperature $t + dt$. Thus, if a kilogramme of a substance in a liquid state, having a temperature t and subjected to a pressure p, be converted into saturated vapour at a temperature $t + dt$ and under a pressure $p + dp$, then the energy of the substance increases by

$$c\,dt + \rho + d\rho.$$

(*b*) Let us bring the given liquid, which is under a pressure p and at a temperature t, wholly into the state of saturated vapour at the same pressure and temperature. The internal energy of the substance is increased by ρ. Let us heat the vapour by dt without altering the volume v. By this means the internal energy is further increased by $k\,dt$, where k is a quantity equal to the specific heat of the vapour at constant volume. The vapour will now be in a superheated state. Let us increase the pressure p, under which it occurs, by dp without changing its temperature $t + dt$; the vapour then passes into a state of saturation. Moreover, if it follows the laws of Boyle and Gay-Lussac, the internal energy of the vapour will not change on compression. If, on the contrary, it does not follow these laws, then the internal energy will decrease by some quantity S, because as a rule the internal energy of substances is decreased by contraction. Hence, in order to convert a kilogramme of a liquid at t and p into vapour at $t + dt$ and $p + dp$, it is necessary (not counting external action) to augment the internal energy of the liquid by

$$\rho + k\,dt - \mathrm{S}.$$

And as both expressions represent one and the same thing, therefore

$$c\,dt + \rho + d\rho = \rho + k\,dt - \mathrm{S},$$

whence

$$d\rho = -(c - k)\,dt - \mathrm{S} *.$$

If it be allowed that *a saturated vapour is, at a certain pressure, subject to the laws of Boyle and Gay-Lussac,* then S = 0, because the energy of a perfect gas is not dependent upon the pressure. This is the fundamental proposition of the present paper; and it is not an arbitrary one,

* Gorny Journal, 1869, vol. ii. p. 389.

but is, on the contrary, proved by calculations and theoretical considerations given below. Under such a state of the vapour we obtain from the preceding equation,

$$d\rho = -(c-k)dt. \quad . \quad . \quad . \quad . \quad . \quad (1)$$

If v denote the specific volume of the vapour in a state of saturation, and if it be supposed that the vapour at this volume and corresponding pressure p and temperature t has the properties of a perfect gas, *i. e.* is subject to the laws of Boyle and Gay-Lussac, we shall have

$$pv = DT*;$$

where $T = 273 + t$ and D is, as is known, a special quantity for every substance when the latter occurs in the state of a perfect gas. The amount of heat required by the vapour in this state for the completion of external work in raising its temperature by $1°$ is equal to AD, where A denotes the thermal equivalent of work. Moreover, if c_1 be the specific heat of the vapour at constant pressure, we have

$$k = c_1 - AD. \quad . \quad . \quad . \quad . \quad . \quad (c)$$

If r denote the latent heat of vaporization and w the specific volume of the liquid, then, as is known,

$$\rho = r - Ap(v-w).$$

Under small pressures w is exceedingly small compared with v; therefore it may be said without any perceptible error that

$$p(v-w) = DT,$$

and consequently

$$\rho = r - ADT,$$
$$d\rho = dr - ADdt. \quad . \quad . \quad . \quad . \quad . \quad (\rho)$$

The equations (1), (c), and (ρ) lead to the following,

$$dr - ADdt = -(c - c_1 + AD)dt,$$

whence it follows that

$$dr = -(c - c_1)dt. \quad . \quad . \quad . \quad . \quad . \quad (2)$$

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* This equation is not exact. D. T. Mendeléeff showed that near a certain pressure, proper to every gas, the latter is subject to Boyle's law; beyond this pressure pv varies with p. The pressure at which pv is constant should fall with a rise of temperature. Let us imagine a saturated vapour and allow it to expand freely at a constant temperature; then, according to Mendeléeff's law, the vapour will attain such a state of rarefaction that it will fully satisfy the equation $pv = $ a constant, and will therefore possess the properties of a perfect gas. It is possible to imagine such an instance, that a vapour will follow Boyle's law even in a state of saturation. Thus the proposition, that a vapour in a state of saturation follows Boyle's and Gay-Lussac's laws near a certain temperature, is in harmony with other well-known phenomena.

The French chemist Bertrand* obtained the same equation, but he avows its inapplicability to liquids. Indeed, according to Regnault†, for water

$$r = 606 \cdot 5 - 0 \cdot 695\, t\, ;$$

whence

$$dr = -0 \cdot 695\, dt.$$

On the other hand, taking $c = 1$ and $c_1 = 0 \cdot 4805$‡, we find

$$dr = -0 \cdot 5195\, dt,$$

which differs considerably from the above. The same disagreement is observed for other liquids. Moreover, for the majority of liquids r is expressed by a trinomial function, and hence the increment of r is not proportional to the increment of temperature, as it should be according to equation (2). But the discordance is completely removed if equation (2) be not referred to vapour at any temperature, but only at that temperature when the vapour is entirely subject to the laws of Boyle and Gay-Lussac. It has been said above that such a temperature does actually exist for aqueous and the majority of investigated vapours, and therefore equation (2) is quite applicable for this and its adjacent temperatures.

Let us take the known equation

$$A\,(v - w)p\,\frac{dp}{dt}\,T = rp.$$

Inasmuch as when a vapour nearly approaches the state of a perfect gas $(v - w)p$ may be taken as equal to DT, therefore it follows from the preceding equation that

$$\frac{\dfrac{dp}{dt}}{p}\,AD = \frac{r}{T^2}. \quad \ldots \ldots \quad (3)$$

If it be supposed that c and c_1 are constants and do not depend upon the temperature, then equation (2) may be integrated:

$$r - r_0 = (c - c_1)\,(T - T_0). \quad \ldots \ldots \quad (4)$$

By T_0 we understand the temperature at which the vapour follows the laws of Boyle and Gay-Lussac; r_0 the latent heat of vaporization at the temperature T_0. On substituting r by the quantity equal to it, deduced from the last

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* *Thermodynamique* par J. Bertrand, 1887, p. 77.
† *Mémoires de l'Académie des Sciences*, t. xxi.
‡ *Idem*, t. xxvi.

equation in (3), we have

$$\mathrm{AD} \cdot \frac{\dfrac{dp}{dt}}{p} = \frac{r_0 - (c - c_1)\,(\mathrm{T} - \mathrm{T}_0)}{\mathrm{T}^2}. \quad . \quad . \quad . \quad (4')$$

If, as before, $c - c_1$ be considered as constant, then this equation can be integrated. By taking T_0 and T_1 at the corresponding p_0 and p_1 as limits, we find, after an easy transposition,

$$\log \frac{p}{p_0} = -\frac{c - c_1}{\mathrm{AD}} \left(\log \frac{\mathrm{T}}{\mathrm{T}_0} - m \frac{\mathrm{T} - \mathrm{T}_0}{\mathrm{T}} \right) + \frac{m r_0}{\mathrm{AD}} \left(\frac{1}{\mathrm{T}_0} - \frac{1}{\mathrm{T}} \right). \quad (5)$$

Here log is Brigg's logarithm, m the modulus ;

$$\log m = \bar{1}\cdot 3622157.$$

J. Bertrand, by assuming that a vapour has the properties of a perfect gas at any temperature, obtained the formula [*]

$$\log p = \alpha - \frac{\beta}{\mathrm{T}} - \gamma \log \mathrm{T}, \quad . \quad . \quad . \quad (6)$$

in which α, β, and γ are arbitrary constants, whose arbitrariness this savant took advantage of in order to bring the pressures calculated from this formula in closest agreement with the results of observation, or, more truly speaking, with those calculated by means of interpolation-formulæ from observed pressures. The expression previously found by A. Dupré for vapour-pressures can be put into the same form.

This investigator, instead of making my assumption as to the constancy of $c - c_1$, took Regnault's empirical formula

$$r = a - bt,$$

and assumed it to be true for all vapours. Then, from equation (3), we have

$$\mathrm{AD} \frac{\dfrac{dp}{dt}}{p} = \frac{a - bt}{\mathrm{T}^2},$$

whence it is easy to obtain a formula of the form (6).

Equation (5) also does not essentially differ from (6). Indeed it can be transformed thus :

$$\log p = \log p_0 + \frac{c - c_1}{\mathrm{AD}} (\log \mathrm{T}_0 + m) + \frac{m r_0}{\mathrm{AD}\,\mathrm{T}_0}$$
$$- \left(\frac{c - c_1}{\mathrm{AD}} \cdot m \mathrm{T}_0 + \frac{m r_0}{\mathrm{AD}} \right) \frac{1}{\mathrm{T}} - \frac{c - c_1}{\mathrm{AD}} \log \mathrm{T}.$$

[*] *Thermodynamique*, p. 92.

This last equation passes into (6) if it be assumed that

$$\log p_0 + \frac{c - c_1}{\mathrm{AD}}(\log \mathrm{T}_0 + m) + \frac{mr_0}{\mathrm{ADT}_0} = \alpha,$$

$$\frac{c - c_1}{\mathrm{AD}} m\mathrm{T}_0 + \frac{mr_0}{\mathrm{AD}} = \beta,$$

$$\frac{c - c_1}{\mathrm{AD}} = \gamma.$$

The difference between the equations (5) and (6) is that the former does not contain any arbitrary magnitudes, as we shall prove subsequently ; while equation (6) contains three arbitrary magnitudes, which Messrs. Bertrand and Dupré [*] endeavour to so choose for each vapour individually that the formula may best accord with the results of experiment. Hence equation (6) is an empirical one, while equation (5) should be regarded as one based upon theory. In order to convince ourselves of this, let us consider the magnitudes which enter into the second portion of equation (5). The specific heats c and c_1 of substances in a liquid and vaporous state can be determined with more or less accuracy by experiment. A is the thermal coefficient of work, we take it as equal to $\frac{1}{425}$; D is a constant quantity for every substance when it occurs as a perfect gas. It is not difficult to prove that

$$\mathrm{AD} = \frac{848 \cdot 7}{425\,\mathrm{P}},$$

or nearly

$$= \frac{2}{\mathrm{P}} ;$$

P is the molecular weight of the vapour. The magnitudes T_0, r_0, and p_0 correspond to that state of a vapour when it is entirely subject to the laws of Boyle and Gay-Lussac. If we have the means of determining the temperature which corresponds to this state of a vapour, then T_0, and consequently r_0 and p_0, become perfectly definite quantities. I shall afterwards give two methods, controlling each other, by means of which it is possible to find such a temperature for any substance if only it exists, and if there be a sufficient number of observations on the vapour-pressure of the substance. Thus *equation* (5) *contains no arbitrary magnitudes* ; and in this it differs from all the formulæ which have been found by

* *Théorie Mécanique de la Chaleur* par Athanase Dupré.   1869.

various savants for the pressure of vapours in a state of saturation.

It must be remembered, however, that equation (5) gives only an approximate value for the vapour-pressure, except for the temperatures T_0 and those adjacent to it, when there can be no difference between the results of calculation and experiment; but at temperatures far removed from T_0 the difference may be very considerable. Recollecting the assumptions and inexactitudes which were allowed in deducing the equation (5), we must acknowledge it to be perfectly applicable: (1) when the vapour, saturating its space, subjects itself to Boyle's and Gay-Lussac's laws, or varies very slightly from them; (2) if $c-c_1$ does not vary with the temperature; (3) if the coefficient of expansion of the liquid be exceedingly small, and the pressure under which it occurs be not abnormally high; and (4) if the volume (w) of the liquid be so small compared with the volume (v) of the vapour formed from it that w may be taken as equal to zero. The first three conditions may be allowed within certain limits of temperature, but the fourth can never be observed with any degree of great accuracy; in the case of small pressures w can be neglected without essential error, but with great pressures this is not allowable. The difference between the results of theory and experiment increases in proportion to the divergence from the above conditions, and in the end they frequently differ entirely.

When the dependence of the pressure of a vapour upon any magnitude whatever is discovered, then it is easy to express the specific volume of a vapour by means of the same magnitude. The equation

$$pv = DT$$

serves for this purpose. Let us also take

$$p_0 v_0 = DT_0 ;$$

whence

$$\frac{v}{v_0} = \frac{T}{T_0} \cdot \frac{p_0}{p},$$

$$\log \frac{v}{v_0} = \log \frac{T}{T_0} - \log \frac{p}{p_0}.$$

On replacing $\log \dfrac{p}{p_0}$ by its magnitude in equation (5) we shall have

$$\log \frac{v}{v_0} = \log \frac{T}{T_0} + \frac{c-c_1}{AD}\left[\log \frac{T}{T_0} - m\frac{T-T_0}{T}\right] + \frac{mr_0}{AD}\left(\frac{1}{T} - \frac{1}{T_0}\right).$$

2. Before applying equation (5) to various liquids we will investigate its properties. The equation may be given in another simpler form, more convenient for calculation. To do this let us resolve $\log \frac{T}{T_0}$ into a series in powers of $\frac{T-T_0}{T}$, and cast aside the members higher than the second power. In this manner we shall have, instead of equation (5), the following :—

$$\log \frac{p}{p_0} = \frac{c - c_1}{2 \mathrm{AD}} \cdot m \cdot \left(\frac{T - T_0}{T}\right)^2 + \frac{m r_0}{\mathrm{AD}}\left(\frac{T}{T_0} - \frac{1}{T}\right). \quad . \quad (5')$$

This equation serves only in the case when the fraction $\frac{T-T_0}{T}$ is small, and when, consequently, the temperature T is not too far removed from T_0; the results given by it will be particularly near to those of experiment if $c - c_1$ be small. I have applied this equation to bisulphide of carbon [12]* in order to form an idea of its accuracy, and found that the simplified equation (5′) and the complete equation (5) give similar, or very nearly similar, results.

Experiments have shown that the difference $c - c_1$ is exceedingly small, compared to the heat of vaporization, for all investigated substances. Therefore the first member of the equation may be neglected, and we shall have

$$\log \frac{p}{p_0} = \frac{m r_0}{\mathrm{AD}}\left(\frac{1}{T_0} - \frac{1}{T}\right). \quad . \quad . \quad . \quad . \quad (r)$$

Whence a formula analogous to that of Roche † can be easily obtained by integration,

$$p = a \alpha^{\frac{t}{1+mt}}.$$

a, α, and m are arbitrary constants. By choosing them in the most advantageous manner Regnault obtained a formula which amply satisfied the results of observation, and which was hardly less satisfactory than Biot's formula with five arbitrary coefficients. The nearer $\frac{c - c_1}{\mathrm{AD}}$ approaches to zero the better does formula (r) agree with the results of experiment. Among the substances for which I made calculations there was one, namely ethyl bromide [14], for which $c - c_1$ closely equalled zero. I calculated its vapour-pressure according to formula (r). Thus Roche's formula has a

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* The figures placed in brackets refer to the numbers of the sections in this paper.
† *Mémoires de l'Acad. des Sci.* t. xxi. p. 585.

theoretical basis ; this explains its accordance with the results
of experiments.

The same formula may be deduced upon other bases.
According to Southern and Crighton's law, the inaccuracy
of which was, however, proved by Regnault's experiments,
the heat of vaporization does not depend upon the pressure on
the surface of a liquid remaining constant at all temperatures.
If this law were true, then instead of equation (4) we should
have the less accurate one

$$r = r_0.$$

Then equation (4′) would be converted into the following:—

$$\frac{\frac{dp}{dt}}{p} = \frac{r_0}{\mathrm{AD}} \cdot \frac{1}{\mathrm{T}^2},$$

whence by integration we obtain equation (*r*).

Thus Southern's inaccurate law and equation (*r*) proceed
from one and the same supposition, that $c - c_1$ is negligible
compared with r. This is sufficiently near the truth, and
may be regarded as the very first approximation.

From the preceding we have the right to conclude that
Roche's formula, although roughly, still presents a law of
nature. All the other empirical formulæ—Young's, Arago's,
Dulong's, Tredgold's, Cariolis', and others, and among them
Biot's—have no theoretical basis, and with the exception of
the latter do not satisfy the results of experiments. It is true
that Biot's formula gives vapour-pressures very nearly ap-
proaching those found by experiment ; but this is not due to
its representing in itself the nature of a vapour, but because
of the large number (five) of arbitrary coefficients, or, in
geometrical language, because the curve expressed by Biot's
formula has a large number (five) of points common to the
curve of the actual vapour-pressures in a state of saturation.

3. Let us investigate the curve expressed by the equation (5),
taking as abscissæ the absolute temperatures T, and as ordi-
nates the pressures *p*. From this formula it is easy to obtain

$$\frac{p}{p_0} = \left(\frac{\mathrm{T}_0}{\mathrm{T}}\right)^x \cdot e^{(y + x\mathrm{T}_0)\left(\frac{1}{\mathrm{T}_0} - \frac{1}{\mathrm{T}}\right)}.$$

Here $x = \dfrac{c - c_1}{\mathrm{AD}}, y = \dfrac{r_0}{\mathrm{AD}}$, and $y + x\mathrm{T}_0$ is a perfectly definite

and constant quantity for every vapour. Let

$$y + x\mathrm{T}_0 = \mathrm{R}.$$

Hence we find

$$\frac{p}{p_0} = \left(\frac{T_0}{T}\right)^x \cdot e^{R\left(\frac{1}{T_0} - \frac{1}{T}\right)}, \quad \ldots \ldots \quad (p)$$

$$\frac{dp}{dt} = p \cdot \frac{R - xT}{T^2}, \quad \ldots \ldots \quad (p_1)$$

$$\frac{d^2 p}{dt^2} = \frac{p}{T^4}\left[x(x+1)T^2 - 2(x+1)RT + R^2\right]. \quad (p_2)$$

It is evident from equation (p) that the curve passes through the origin of the coordinates, and from equation (p_1) that the curve touches the axis of abscissæ at this point. From equation (p_2) it follows that $\frac{d^2 p}{dt^2}$ becomes zero twice as T rises from zero,

when $T_1 = \frac{R}{x}\left(1 - \frac{1}{\sqrt{x+1}}\right)$, and when $T_2 = \frac{R}{x}\left(1 + \frac{1}{\sqrt{x+1}}\right)$.

From $T = 0$ to $T = T_1$,

$$\frac{d^2 p}{dt^2} > 0.$$

From $T = T_1$ to $T = T_2$,

$$\frac{d^2 p}{dt^2} < 0.$$

When $T > T_2$,

$$\frac{d^2 p}{dt^2} > 0.$$

$\frac{dp}{dt}$ becomes zero when $T = \frac{R}{x}$, then

$$\frac{d^2 p}{dt^2} < 0;$$

consequently p then attains its maximum. Thus, starting from the origin of the coordinates, the curve diverges from the axis of abscissæ and turns its convexity towards it. When $T = \frac{R}{x}\left(1 - \frac{1}{\sqrt{x+1}}\right)$ an inflexion takes place; the curve turns its concavity towards the axis of abscissæ; p continuing to augment attains a maximum when $T = \frac{R}{x}$. Then p decreases; a second inflexion occurs, and then the curve asymptotically approaches the axis of abscissæ. For the subject under consideration the entire curve is not of importance, but only that

inconsiderable portion of it between the origin of coordinates and the first inflexion, beyond which observations are never carried. Moreover, it must be remembered that the formula under consideration refers only to certain special conditions, one of which is never actually fulfilled, namely—that the volume of a liquid is equal to zero compared to the volume of the vapour formed from it, so that the curve represented by equation (p) serves to express the actual variation of the pressure of a vapour, and would only fully express these variations if the above conditions were strictly observed [*].

The temperature of the first point of inflexion is very high. For water, for instance [†],

$$R = 5106 \cdot 2 + 5 \cdot 2948 \times 343 = 6922 \cdot 3 ;$$
$$T_1 = \frac{6922 \cdot 3}{5 \cdot 2948} \left(1 - \frac{1}{\sqrt{5 \cdot 2948}} \right) = 844° \cdot 8.$$

The highest temperature of steam attained by Regnault was only 230°. So also it is easy to find that for sulphuric ether the first inflexion of the curve corresponds to 743°·2, for benzene 886°·7, sulphur 1279°.

With the majority of the substances I calculated for, x is a positive quantity, but it is sometimes negative and may be equal to zero; R was always positive. If $x < 0$, when its absolute magnitude > 1, then it is easy to prove, from the above-mentioned equations (p), (p_1), and (p_2), that as T varies from zero to infinity, the curve diverges continuously from the axis of abscissæ, and always turns its convexity towards this axis, without giving any special points.

We may add that it would be absurd to deduce any properties of a vapour from the properties of the curves and

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[*] My paper "On Van der Waals' Formula" (Russian Physico-Chemical Society, vol. xix.) proves that for all substances the second differential coefficient $\frac{d^2p}{dt^2}$, where p is a function of v and t, is greater than zero, and that it is only for perfect gases that $\frac{d^2p}{dt^2} = 0$. This may seem a contradiction to the above, because the value of $\frac{d^2p}{dt^2}$ for the curve (5) is either less or equal to zero. In reality there is no contradiction at all. To be concise, I will only observe that the curve expressed by equation (p) presents the variation of the vapour-pressure under certain conditions and within certain limits; in the given instance it only applies for that portion of the curve which lies between the origin of coordinates and the first point of inflexion, and then the condition that $\frac{d^2p}{dt^2} > 0$ is fulfilled.

[†] In order to calculate R and T_1 it is necessary to know x and T_1; the mode of determining these quantities is given below. For water $x = 5 \cdot 2948$, $T_0 = 343°$ [6].

equation (5) we have just considered, because they do not refer to actual vapours but only to imaginary ones such as do not really exist.

4. I will now pass to the applications of equation (5) and to proving that its theoretical bases are confirmed by experiment. The fundamental proposition upon which equation (5) is based is that at a certain temperature a vapour in a state of saturation has the properties of a perfect gas. Above and below this temperature it diverges from these properties, but for the present investigation it does not matter in which direction. It follows from the calculations given below that such a temperature does actually exist for the majority of substances yet experimented upon, and which are liquids at the ordinary temperature and pressure. The vapours of other liquids are not subject to the laws of Boyle and Gay-Lussac within the limits of the observations made by us. Without fresh observations it is impossible to say if these vapours are able to exist in the state of a perfect gas outside the temperatures observed. Equation (5) is naturally as yet inapplicable to such vapours. Our theory should not be applied to gases which are able to take the form of liquid only under very high pressures, because the volume of the resultant liquid would then be somewhat considerable compared with the volume of the gas and could not, therefore, be taken as zero, as our theory demands.

5. Suppose that in equation (5)

$$\frac{c - c_1}{A D} = x, \quad \frac{r_0}{A D} = y,$$

we shall have

$$\log \frac{p}{p_0} = - \left[\log \frac{T}{T_0} - m \frac{T - T_0}{T} \right] x + \left(\frac{1}{T} - \frac{1}{T_0} \right) m y. \quad (7)$$

If x and y be regarded as arbitrary constants, then they might be determined, if any vapour-pressures p, p_0, and p_1 were known corresponding to temperatures T_1, T_0, and T'. If, moreover, vapours in a state of saturation followed Boyle's and Gay-Lussac's laws, and if in general the propositions which served for the deduction of equations (5) or (7) were unimpeachable and perfectly accurate, then the pair of unknown quantities x and y would be the same whatever were the temperatures T_1, T_0, and T', and their corresponding tensions p_1, p_0, and p'. In reality just the contrary occurs. Every three observations, taken at random, give in general different magnitudes for x and y, so that not unfrequently

there is no similarity between two pairs of these magnitudes. And so it should be, because equation (5) can only be applied with the observation of certain conditions, which generally speaking are not fulfilled. Nevertheless, it is possible with nearly all liquids to find a temperature T_0 which has such properties that the magnitudes x and y are approximately the same whatever three temperatures are taken, if only they are adjacent to T_0 and to each other. We will now turn our attention to determining this temperature. I have discovered two methods, which are here given, and for the sake of clearness applied to aqueous vapour.

6. Let us take three adjacent temperatures, T_1, T_0, and T', differing for instance by $5°$, so that $T'-T_0=T_0-T_1=5$, and calculate the values of x and y. Then let us calculate their values for three other temperatures as near as possible to the first; and then for three more temperatures, and so on; and thus combine a more or less considerable number of observations. We thus obtain values for x and y which are different, but with the majority of substances *experimented* upon (*i. e.* for which there are tables of vapour-pressures, in a state of saturation, x, varying uninterruptedly with the corresponding temperatures) give a maximum or minimum value. If the mean (intermediate) of the temperatures T_0 be laid along the axis of abscissæ, and x along the axis of ordinates, then a curve is obtained with a maximum or minimum. There are, however, vapours for which the curve of x's continuously recedes from or approaches the axis of abscissæ with a rise of temperature; the path of the curve indicates where the maximum or minimum lies, beyond the greatest or least of the temperatures observed.

The value of $c-c_1$ varies very inconsiderably within small limits of temperature; therefore, the magnitude x should remain constant, whatever combination of temperatures be taken, at temperatures near to that at which the vapour has the properties of a perfect gas, and when in general the above theory stands good; and this is only possible when x has a value near to its maximum or minimum[*], because a considerable variation in T then produces an inconsiderable variation in x. Hence the desired temperature T_0 is that at which x has a maximum or minimum value. We may here remark that at this time y varies with the temperature, as is seen from equation (4); or, more accurately, the increment of y is equal to x multiplied by the increment of temperature.

[*] I do not consider the case when the curve has an inflexion whose direction is parallel to the axis of abscissæ, because I have not met with such an instance in my investigations upon vapours.

If x has no maximum or minimum, then the vapour does not possess the properties of a perfect gas at any temperature, within the limits of observation, and the theory is not applicable to it. Then y does not vary proportionally to the temperature.

To calculate the values of x and y it is sufficient to have two equations and three observed tensions corresponding to three temperatures. For the sake of simplicity let us take equidistant temperatures :—

$$T - T_0 = T_0 - T_1 = \Delta.$$

We shall thus have two equations of the first degree with two unknown quantities :—

$$-\left(\log\frac{T_0}{T_1} - m.\frac{T_0 - T_1}{T_0}\right)x + \left(\frac{1}{T_1} - \frac{1}{T_0}\right)my = \log\frac{p_0}{p_1},$$

$$-\left(\log\frac{T_1'}{T_0} - m.\frac{T' - T_0}{T'}\right)x + \left(\frac{1}{T_0} - \frac{1}{T_1}\right)my = \log\frac{p'}{p_0}.$$

On solving them we obtain

$$x = -\frac{T_1\log\dfrac{p_0}{p_1} - T'\log\dfrac{p'}{p_0}}{T_1\log\dfrac{T_0}{T_1} - T'\log\dfrac{T'}{T_0}}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

$$y = -T_0 x - \frac{\left(\log\dfrac{T'}{T_0}.\log\dfrac{p_0}{p_1} - \log\dfrac{T_0}{T_1}\log\dfrac{p'}{p_0}\right)T_1 T_0 T'}{\left(T_1\log\dfrac{T_0}{T_1} - T'\log\dfrac{T'}{T_0}\right).\Delta} \quad . \quad . \quad (9)$$

To obtain x to a sufficient degree of accuracy, the three temperatures for which this value is calculated must be taken as near as possible to one another, because the direction of the curve of x's can only be looked upon as parallel to the axis of abscissæ, near the maximum and minimum, for an inconsiderable distance. Moreover, this requires exceedingly careful observations of the vapour-pressures, as otherwise the series of values of x present such irregularities as to prevent the possibility of distinguishing the maximum or minimum of this quantity. These irregularities become less perceptible as the difference of temperature increases and the order of the variation of the x's becomes clearer ; but in this case, according to what has been said above, the maximum or minimum value of x and the corresponding temperature may prove

insufficiently accurate. Let us apply equation (8) to aqueous vapour and take, at random, temperatures 40°, 45°, and 50°. If we take the temperature of absolute zero as −273°, then these temperatures counted from the absolute zero will be 313°, 318°, and 323°, and the corresponding pressures calculated by Broch[*] according to Regnault's observations, 54·8651 millim., 71·3619 millim., and 91·9780 millim. On substituting these figures in equation (8) we find

$$x_{45} = 3·9542.$$

In this, and in all further calculations, x refers to the intermediate temperature, and we now mark x_{45} by the number 45. In a like manner we find for temperatures 45°, 50°, and 55°,

$$x_{50} = 4·3293.$$

Below is a table in which the upper line contains the intermediate temperatures (t) and the lower the corresponding values of x :—

t	45°	50°	55°	60°	65°	70°	75°	80°
x	3·9542	4·3293	4·6800	5·0031	5·2109	*5·2948*	5·1997	3·8844

In this series of figures the greatest value of x is 5·2948, corresponding to 70° ; x diminishes with a rise and fall of temperature, at 15° it is 2·0640 and at 125° 3·4263. Hence it is evident that near 70° aqueous vapour follows the laws of Boyle and Gay-Lussac ; *i. e.* satisfies the equation

$$pv = DT.$$

If in the equation

$$\frac{c - c_1}{AD} = x$$

we replace x and AD by their values, we have

$$c - c_1 = x \cdot AD = 5·2948 \cdot \frac{2}{P} = 5·2948 \cdot \frac{2}{18} = 0·58831.$$

The specific heat c as determined by various experimenters shows a great diversity. According to Regnault c at 70° equals 1·0072, while according to Hendrichsen it is 1·0419. The value of c_1 was determined by Regnault for temperatures above 100°, at 70° it is probably less. Thus, according to Regnault $c - c_1 = 0·5167$, and according to Hendrichsen it is 0·5614. The latter more nearly approximates to that found

[*] *Physikalisch-chemische Tabellen von Landolt und Börnstein*, § 18.

above, 0·58831, and would be still nearer if a smaller figure were taken instead of 0·4805.

On making the requisite substitutions in equation (9) we find that

$$y = 5106 \cdot 2,$$

whence

$$r_0 = y \cdot AD = 5106 \cdot 2 \cdot \frac{2}{18} = 567 \cdot 36.$$

According to Regnault's well-known formula we find that the latent heat of vaporization at 70°,

$$r_{70} = 557 \cdot 6.$$

The difference between the values of r_0 and r_{70} is less than 2 per cent. The accordance between the results of theory and experiment must be regarded as fully satisfactory if we take into consideration the imperfect observation of the requisite conditions and especially the inexactitude of the experimental determinations of the amount of heat. If instead of 70° we take a temperature which is considerably higher or lower, then the results are less accordant; thus at 125° we find 542·8 for the latent heat according to equation (9), while, according to Regnault, $r_{125} = 519 \cdot 6$. The value of $c - c_1$ will then be 0·3807, which diverges still more from the results of experiment.

7. We will now consider the second mode of calculating r_0 and $c - c_1$. It follows from equation (3) that

$$r = \frac{AD \cdot T^2 \dfrac{dp}{dt}}{p}. \quad . \quad . \quad . \quad . \quad . \quad (10)$$

This equation gives the possibility of calculating the heat of vaporization if it be assumed that the vapour follows the laws of Boyle and Gay-Lussac, and that in general the above enunciated theory contains no inexactitudes. But in order to make this calculation it is necessary to know the first differential coefficients of pressure $\dfrac{dp}{dt}$, the determination of which, however, presents considerable difficulty. If this quantity, at T and p, be taken as equal to the difference between p and the pressure answering to the temperature $T - \Delta$, divided (*i.e.* the difference) by Δ, then we find that $\dfrac{dp}{dt}$ is too small, while if we take the temperature $T + \Delta$ it is too great. Generally the arithmetical mean of these two

values is taken, but still it is far from being the true value, and the difference is greater the more rapidly p varies. In order to lessen the error it is necessary to make use of more or less complex interpolation formulæ. Let

$$p = a + a_1 T + a_2 T^2,$$

where a, a_1, a_2 are arbitrary constants which may be calculated from three observations. Hence

$$\frac{dp}{dt} = a + 2a_2 T' ;$$

this equation only leads to the above method, which, as we saw, was not sufficiently accurate. In order to attain a greater degree of accuracy, let us take the more complex formula

$$p = a + a_1 T + a_2 T^2 + a_3 T^3 ; \quad \cdots \quad \cdots \quad \text{(T)}$$

the four arbitrary constants are determined from four observations. Hence we have

$$\frac{dp}{dt} = a_1 + 2a_2 T + 3a_3 T^3.$$

Let the vapour-pressures corresponding to the temperatures T_1, T_2, T_3, and T_4 be p_1, p_2, p_3, and p_4; we will denote the differential coefficients corresponding to these pressures thus:—

$$\frac{dp_1}{dt}, \quad \frac{dp_2}{dt}, \quad \frac{dp_3}{dt}, \quad \frac{dp_4}{dt}.$$

We will assume that tables of vapour-pressures are formed for equal intervals of temperature, so that

$$T_4 - T_3 = T_3 - T_2 = T_2 - T_1 = \Delta.$$

On substituting the pressures p_1, p_2, p_3, and p_4 with their corresponding temperatures in equation (T), we obtain four equations, from which, after a very easy transmutation, we find

$$\left.
\begin{aligned}
\frac{dp_1}{dt} &= \frac{2(p_4 - p_3) - 7(p_3 - p_2) + 11(p_2 - p_1)}{6\Delta} \\[2mm]
\frac{dp_2}{dt} &= \frac{-(p_4 - p_3) + 3(p_3 - p_2) + 2(p_3 - p_1)}{6\Delta} \\[2mm]
\frac{dp_3}{dt} &= \frac{2(p_4 - p_3) + 3(p_3 - p_2) - (p_2 - p_1)}{6\Delta} \\[2mm]
\frac{dp_4}{dt} &= \frac{11(p_4 - p_3) - 7(p_3 - p_2) + 2(p_2 - p_1)}{6\Delta}
\end{aligned}
\right\} \quad \cdots \quad \text{(11)}$$

Each value of $\frac{dp}{dt}$ can be calculated four times :—(1) we may regard it as corresponding to the pressure p_1 followed by three other pressures, p_2, p_3, and p_4, and therefore calculate it from the first of equations (11) ; (2) we may suppose that $\frac{dp}{dt}$ corresponds to the pressure p_2 which is preceded by one value p_1, and followed by two, p_3 and p_4, and therefore the differential coefficient must be calculated as $\frac{dp_2}{dt}$, *i. e.* from the second of the equations (11) ; (3) when the pressure p is preceded by two and followed by one pressure, then $\frac{dp}{dt}$ must be calculated from the third of the equations (11) ; and, lastly, (4) the differential coefficient is calculated from the equation for $\frac{dp_4}{dt}$. If the figures forming a table follow some definite law, then the values of the differential coefficient, although determined by different methods, should be similar and differ only in the inevitable errors of observation ; or, more strictly speaking, of calculation, because all tables of vapour-pressures are found by means of interpolation formulæ. If the differences are great it shows that in one figure, at least, there is a misprint or error exceeding the possible one. The tables of vapour-pressures which I investigated nearly always gave four very nearly similar values of $\frac{dp}{dt}$. Considerable discordances enabled me to discover misprints or errors in the tables. I may here remark that irregularities in the values of x, calculated by the first method, also sometimes revealed an error in observation.

In all the calculations the results of which are given below, I did not calculate the differential coefficient four times, but only twice by means of the formulæ $\frac{dp_2}{dt}$ and $\frac{dp_3}{dt}$, and took the arithmetical mean of the results.

Knowing how to find the differential coefficient $\frac{dp}{dt}$, it is possible to calculate the heat of vaporization r for each temperature according to equation (10). Let us endeavour to determine the temperature with whose uniform rise or fall the value of r also uniformly varies, so that if the tempera-

ture varies constantly by Δ, then r varies by one and the same quantity $(c - c_1)\Delta$ by equation (2). This temperature will evidently be that same T_0 which was found by the first method. It should, however, be remarked that $(c - c_1)\Delta$ is exceedingly small compared to r; therefore, in order to obtain results approaching those of experiment, it is necessary to have very exact tables, accurate to tenths, and with small pressures to even hundredths of a millimetre. But it is more than difficult to calculate to such a degree of accuracy, and therefore it is best to employ the first method for determining T_0 and to employ the second method as a control.

We will apply the second method to aqueous vapour. Broch has recalculated Regnault's observations on aqueous vapour to four points of decimals. I take from them 9 pressures for 9 temperatures: for the above determined $70°$ and four above and below it, and I calculate $\frac{dp}{dt}$ by means of the second and third of equations (11). The results are given in the following table; the temperature t in the first column, the pressure p in the second, and the differential coefficient $\frac{dp}{dt}$ in the third.

$t.$	$p.$	$\frac{dp}{dt}.$	$t.$	$p.$	$\frac{dp}{dt}.$
$\overset{\circ}{50}$	91·9780		$\overset{\circ}{75}$	288·7640	12·107
55	117·5162		80	354·8730	14·388
60	148·8848	6·923	85	433·1938	
65	187·1028	8·402	90	525·4676	
70	233·3079	10·122			

I consider it not superfluous to explain how I found $\frac{dp}{dt}$.

I calculate this quantity for $60°$, regarding it as $\frac{dp_3}{dt}$ (11) according to the data for temperatures $50°$, $55°$, $60°$, and $65°$. The figure $6·9247$ is obtained. I calculate the same quantity after formula $\frac{dp_2}{dt}$ by means of the pressures corresponding to

the temperatures 55°, 60°, 65°, and 70°. I find 6·9207. The arithmetical mean of these two results is 6·9227 ; the last two figures may contain an error. I take the differential coefficient $\frac{dp}{dt}$ for 60° as equal to 6·923, where an error may be suspected in the last figure ; the result thus obtained is placed in the third column opposite to 60°. In exactly the same way I calculated the differential coefficient $\frac{dp}{dt}$ for 65°, regarding it as $\frac{dp_3}{dt}$ and as $\frac{dp_2}{dt}$; in the first instance I obtained 8·4044, and in the second 8·4002 * ; the mean 8·402 is placed in the table opposite 65°. The other differential coefficients for temperatures 70°, 75°, and 80° were determined in the same manner ; each of them is the arithmetical mean of two figures.

By placing the resultant values of the differential coefficient in equation (10), I calculated the heat of vaporization for five temperatures t ; these results are placed in the second line.

t	60°		65°		70°		75°		80°
r	572·91		570·04		567·13		564·18		561·36
		2·87		2·91		2·95		2·82	
$c-c_1$	0·574		0·582		0·590		0·564	

The figure 567·36 was found for the heat of vaporization at 70° according to the first method ; it may be considered as coinciding with that now found by another method, 567·13. From the tables it is seen that the heat of vaporization falls with a rise of temperature. The third line gives the difference between the two adjacent values of r. These differences are near to each other, but are not equal, as would be expected ; but on following out the calculation it is easily seen that the second decimals in the heat of vaporization, and hence also those figures in the differences, may contain errors depending upon errors in the pressures. The fourth line of the table contains $c-c_1$; these values are obtained by dividing the differences (figures in the third line) by 5. They and their arithmetical mean, 0·578, may be said, taking into consideration the possible errors, not to differ from that found above by more than 0·58831.

When the coefficients of r and x are known, the pressures

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* The figures for one and the same coefficient differ constantly by the two last figures (3rd and 4th). This is due to the inaccuracy of the figures of the pressures; hence the labour expended by Broch in their calculation may be counted as fruitless.

of aqueous vapour may be calculated by means of equation (5) or (7), which in the given instance takes the form

$$\log \frac{p}{233 \cdot 09} = - \left[\log \frac{T}{343} - m \frac{T - 343}{T} \right] 5 \cdot 2948$$
$$+ m \left[\frac{1}{T} - \frac{1}{343} \right] 5106 \cdot 2.$$

In the following table the temperatures t are placed in the first column, the pressure of aqueous vapour in millimetres, in a state of saturation and calculated by means of equation (7), in the second column, and the pressures according to Regnault's observations in the third column[*].

t.	Pressures.			
	Calculated from equation (7).	Observed.	Calculated from equation (5_2).	Calculated from equation (5_1).
−30°	0·358	0·386	0·510	1067·15
−20	0·891	0·927	1·170	817·03
−10	2·053	2·151	2·519	817·03
0	4·408	4·569	5·120	428·28
10	8·949	9·140	9·936	428·28
20	17·159	17·363	18·392	187·55
30	31·334	31·510	32·692	187·55
40	54·74	54·87	56·01	94·84
60	148·86	148·88	149·20	150·15
80	354·92	354·87	355·70	353·47
100	758·65	760·00	772·56	704·61
140	2669·4	2717·6	2908·9	1851·54
180	7187·7	7546·5	8667·0	1851·54
220	15864·8	17390·4	21629·0	5921·18

In this table the temperatures 65°, 70°, and 75° are omitted, because at these temperatures there can be no difference between the results of calculation and observation, as they appertain to points through which both curves pass; that is, both the curve expressed by equation (7) and that representing the actual variation of the vapour-pressure. The curves, which almost accord between the common points, diverge as they become more remote from them, but in their general properties they diverge very slowly, as is indeed seen from the table. Such temperatures as 40°, 60°, and 80°, for which the pressures are calculated after equation (7) and determined by observation, may be considered as equal. At higher and lower

* The meaning of the figures in the 4th and 5th columns will be explained presently.

temperatures the divergence increases, especially on the side of a rise in temperature. This signifies that aqueous vapour in a state of saturation follows Boyle's and Gay-Lussac's laws near 70°, and diverges from these laws at a certain distance from 70°. Other causes still further increase the divergence. Thus $c - c_1$ should remain constant according to our assumption, instead of which both specific heats, especially c, vary with the temperature. The volume of water (w) is taken as equal to zero, which in reality is never the case. These facts have their significance, especially for high pressures, because with water c at low temperatures varies very little, and the volume of liquid (w) is then minute compared to the volume of vapour (v). For this reason, probably, the theory and experiments agree better for low pressures than for high.

8. The determination of x and y from experimental data may lead to the idea that these quantities are arbitrary, and that therefore formula (5) or, which is the same, (7), can be numbered among empirical formulæ. Such a conclusion would, however, not be right ; x and y have each a perfectly definite physical value, and calculated by the above methods prove, at least y does, in the case of water and of other liquids subsequently considered by me, to be near those values given by experiment. If there be not an entire agreement, it may be ascribed to the insufficient accuracy of the methods by means of which the heat of vaporization and specific heats are determined, while the calculation of these quantities, or, which is the same, of x and y, depends according to our theory upon the vapour-pressures, which may be measured with incomparably greater accuracy. This even affords the possibility, although for one temperature T_0 only, of obtaining these quantities for substances which have not been investigated in this aspect. The inexactitude of x and y determined by experiments from the quantities $c - c_1$ and r, moreover, proceeds from the fact that we do not know accurately the values of A, D, and the temperature of absolute zero. We may add that if, instead of the calculated values of $c - c_1$ and r, we take those which are given by experiment, then the tensions calculated after equation (5) approximate to those given by observation, although not so closely as the same values determined by the above mentioned methods. Thus, although the quantities x and y are calculated like arbitrary constants in empirical formulæ, they are not arbitrary, because they have a definite physical meaning and approximate to those values which are given by experiment, and can even be replaced by the latter in equation (7). It

has already been explained that T_0 is also not arbitrary, because this number has a physical significance, and r_0 and p_0, being dependent upon T_0, are therefore also not arbitrary.

Thus, as was said above (§ 1), formula (5) does not contain any arbitrary quantities.

9. I foresee the possibility of yet another objection. Let us imagine two curves of a different nature, and, by the aid of differential coefficients, bring three points of one curve into coincidence with three points of the other curve ; and let us, moreover, assume that these common points approach each other for an infinitely small, or at least exceedingly small, distance. According to the common property of curves, they diverge very gradually as they pass from the three common points, and only diverge to a great extent at a very remote distance from the common points. From this it might be concluded that the fact of the curve (7) and the curve of the actual vapour-pressures being near each other about the common points, and even at a considerable distance from them, does not prove the truth of the above theory. Such a view would be unfounded. In order to prove this, let us take any formula with three arbitrary coefficients, for instance the parabolic formula

$$p = a + a_1 T + a_2 T^2, \quad . \quad . \quad . \quad . \quad (5_1)$$

and assort the constants a, a_1, and a_2 in such a manner that the formula would satisfy temperatures $65°$, $70°$, and $75°$; *i. e.* so that the curve expressed by formula (5_1) would pass through three points lying on the curve (5) and on the curve of the actual vapour-pressures. It is then seen that

$$a = 18513 \cdot 75, \quad a_1 = 116 \cdot 7576, \quad a_2 = 0 \cdot 185020.$$

The vapour-pressures calculated according to formula (5_1) are given in the 5th column of the preceding table. We see that even at temperatures near $70°$, for example at $40°$ and $100°$, the figures in this column differ considerably from those of observation, and at remote temperatures, for instance $20°$ and $220°$, there is not the slightest analogy. Thus formula (5_1) has nothing in common with that function which expresses the dependence of a vapour in a state of saturation on the temperature.

The properties of Roche's formula (§ 2) are different; having a theoretical basis, it somewhat closely satisfies the results of observation. A formula analogous to it may, as we saw, be obtained from the equation

$$\log \frac{p}{p_0} = my \left(\frac{1}{T_0} - \frac{1}{T} \right).$$

On placing the known values of y and T_0 in this formula, we shall have

$$p = p_0 e^{\frac{y(t-70)}{(353)^2[1+(t-70)/353]}},$$

or

$$p = a\alpha^{\frac{t-70}{1+m(t-70)}}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (5_2)$$

where

$$\log a \;\; = 2 \cdot 36793,$$
$$\log \alpha \;\; = 0 \cdot 018849,$$
$$\log m \;\; = \overline{3} \cdot 46471.$$

In Regnault's formula* these figures have another value, because he gives his formula a different aspect, somewhat diverging from theory :

$$p = a\alpha^{\frac{t+20}{1+m(t+20)}},$$

and he endeavours to assort such values for a, α, and m as would best satisfy the results of observation.

Equation (5_2) *contains no arbitrary coefficients* ; it passes through three points common to curve (5), whose abscissæ are 338°, 343°, and 348°. The pressures calculated from this formula are given in the 4th column of the preceding table. Although they agree less with the results of experiment than the figures in the 3rd column, nevertheless it is clear Roche's formula roughly and approximately expresses a law of nature.

Ether, $C_4H_{10}O$.

10. We will now apply our theory to various liquids and commence with ether.

1st Method.

It is seen from the table given below, where the first line represents the temperatures (t) and the second the values of x calculated after formula (8), that the maximum value of x corresponds to 60°.

t	10°	35°	55°	60°	65°	85°	100°
x	0·2821	1·8727	2·6274	*2·77986*	2·7258	2·0899	0·20548

Above and below this temperature x becomes less, and below 10° it is even negative.

For ether,

$$AD = \frac{2}{P} = \frac{2}{74}.$$

We find from the equation

$$\frac{c-c_1}{\text{AD}} = x$$

that

$$c - c_1 = x \times \text{AD} = 2 \cdot 77986 \times \frac{2}{74} = 0 \cdot 07513.$$

According to Regnault $c_{60} = 0 \cdot 56451$, $c_1 = 0 \cdot 47966$; $c - c_1 = 0 \cdot 08485$ *. The difference between these two values is considerable, but a closer agreement is not to be expected, for with the existing calorimetric methods the specific heats of liquids, and especially of their vapours, may contain great errors, so that it is doubtful whether they would impose confidence if they were near to each other—to the difference of their $c - c_1$: if, for example, the second figures (*i. e.* the hundredth parts) of c and c_1 contained errors, then in the difference $c - c_1$ the error would be in the first figure, and consequently the figure found by subtracting c_1 from c would have no scientific value. Errors in the third figures have, although a less, still a great influence on the accuracy of $c - c_1$. Therefore it is better to determine c_1 by means of x than by the usual calorimetric method. Taking $c = 0 \cdot 56451$ and $c - c_1 = 0 \cdot 07513$, we find that $c_1 = 0 \cdot 48938$; this value deserves greater confidence than $0 \cdot 47966$, found by Regnault from experiment.

After making the necessary substitutions in equation (9) we obtain

$$y = 3318 \cdot 74,$$

and further

$$r_0 = 3318 \cdot 74 \times \frac{2}{74} = 89 \cdot 688.$$

I calculated from Regnault's formula that

$$r_{60} = 86 \cdot 196.$$

Although there is not an entire coincidence in the results of calculation and observation, still one cannot but acknowledge that the figures are very similar.

2nd Method.

We take the vapour-pressures corresponding to $60°$ and six adjacent temperatures, and calculate the differential coefficient $\frac{dp}{dt}$ by equation (11).

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* All the data found by Regnault which are here and afterwards inserted are chiefly taken from Landolt's tables; the same may be said concerning the data of other observers.

$t.$	$p.$	$\dfrac{dp}{dt}.$	$t.$	$p.$	$\dfrac{dp}{dt}.$
$\overset{\circ}{45}$	1074·15		$\overset{\circ}{65}$	1998·87	57·912
50	1264·83		70	2304·90	
55	1481·06	45·946	75	2645·41	
60	1725·01	51·707			

From whence by means of equation (10) we construct the table :

t	$50°$		$60°$		$65°$
r	90·203		89·836		89·456
		0·367		0·380	
$c-c_1$......		0·0734		0·0760	

According to the first method we found $r_0 = 89·688$, and according to the second method $= 89·836$; notwithstanding their different origin these figures may be considered the same. The values of $c-c_1$ also proved to be very similar; according to the 1st method 0·0751, and the mean of the two quantities found by the 2nd method 0·0747. All this indicates the truth of the propositions serving as the base of the theory.

Knowing x and y, it is possible to calculate the vapour-pressure of ether by equation (7), which in this instance takes the form

$$\log \frac{p}{148·79} = - \left[\log \frac{T}{333} - m \frac{T-333}{T} \right] 2·77986$$
$$+ m \left[\frac{1}{T} - \frac{1}{333} \right] 3318·74.$$

$t.$	Pressures.		$t.$	Pressures.	
	Calculated.	Observed.		Calculated.	Observed.
$-\overset{\circ}{20}$	65·81	68·90	$\overset{\circ}{70}$	2307·7	2304·9
0	182·03	184·39	0	3891·1	3898·3
20	432·14	432·78	110	6257·5	6214·6
40	907·59	907·04	120	7617·3	7719·2
50	1265·70	1264·8			

This table shows that from 0° to 110° the results of calculation and observation are sufficiently near to each other; hence the vapour of ether in a state of saturation diverges but little between these temperatures from the laws of Boyle and Gay-Lussac.

Benzene, C_6H_6.

11. *1st Method.*

t	30°	55°	70°	75°	80°	85°
x	9·3901	3·8215	2·7054	2·5321	2·5988	2·3905

t	90°	95°	100°	105°	125°	
x	2·5563	2·6051	2·6575	2·7598	3·3561	

In this instance x has not a maximum value, as it has with water and ether, but a minimum, whose exact position it is unfortunately difficult to determine, probably owing to errors (misprints?) in the pressures. It may be said that the minimum lies between 80° and 90°; we will take 85°, and will consider the minimum of x as the arithmetical mean of its three values for temperatures 80°, 85°, and 90°, that is as 2·5152. Hence

$$c - c_1 = 2·5152 \times \frac{2}{78} = ·064492.$$

According to Wiedemann $c_1 = 0·3325$, and Regnault gives $c = 0·43602$, hence $c - c_1 = ·10352$; the disagreement between the above results is explained by the uncertainty of the calorimetric measurements. If, however, we assume that the error in c is small, and take $c - c_1 = ·064492$ as found by the 1st method, then we obtain $c_1 = 0·37153$, which is slightly greater than that determined by Wiedemann. To calculate y, I made three replacements, in equation (9), for x: 2·5988, 2·3905, and 2·5563, corresponding to temperatures 80°, 85°, and 90°, and obtained three figures whose mean was taken as the desired value of y. It appeared that

$$y = 3816·72,$$

whence

$$r_0 = 3816·72 \times \frac{2}{78} = 97·866.$$

According to Regnault $r_{85} = 90·75$ *.

* It is important to exactly calculate the amount of heat required to heat a kilogram of the liquid from 0° to 85°, because observations were not carried beyond 71°.

2nd Method.

t.	p.	$\dfrac{dp}{dt}$.	t.	p.	$\dfrac{dp}{dt}$.
65°	463·43		85°	874·63	26·049
70	547·42		90	1012·75	29·233
75	643·18	20·405	95	1167·40	
80	751·86	23·105	100	1340·05	

t	75°	80°	85°	90°
r	98·517	98·188	97·877	97·526
		0·329	0·311	0·351*
$c-c_1$		0·0658	0·0622	0·0702

The mean value of $c-c_1$ from the three figures of the last line, 0·0661, is very near to that found above, 0·0645, and the heat of vaporization 97·877 to 97·866.

The following table of the vapour-pressures of benzene is calculated from the values of x and y determined above.

t.	Pressures.			t.	Pressures.		
	Calcu-lated.	Ob-served.			Calcu-lated.	Ob-served.	
−20......	8·83	5·79	9·01	70......	547·42	547·42	548·66
−10......	16·28	12·92	16·57	80......	751·84	751·86	752·38
0......	28·59	25·31	29·04	90......	1012·72	1012·75	1012·02
10......	48·14	45·25	48·76	100......	1340·00	1340·05	1337·20
20......	77·84	75·65	78·71	130......	2827·0	2824·4	2811·4
40......	184·43	183·62	185·78	170......	6413·7	6340·7	6348·6
60......	390·19	390·10	391·70				

Owing to the irregularities in the values of *x*, I took the arithmetical mean of three of its values in order to obtain a more reliable result. This may give rise to a mistrust in the figures subsequently determined. In order to test to what

* See Notes at end.

extent they deserve confidence, I recalculated the observations through intervals of 10°.

t	50°	60°	70°	80°	90°	100°
x	3·6539	3·3633	2·4643*	2·5307	2·5271	2·6685

The minimum value of x lies between 80° and 90°. But as the values of x at these temperatures are nearly equal, it is best to take their arithmetical mean and to take the corresponding temperature as 85°. We then have

$$x = 2\cdot5289,$$
$$y_{80} = 3829\cdot5,$$
$$y_{90} = 3803\cdot4,$$

the mean of $y = 3816\cdot5$.

The value now found for x is near to that given above, and the values obtained for y by both methods can be considered as perfectly equal. The pressures calculated from these new values of x and y are given in the fourth column of the preceding table; they differ but little from those in the second column.

Bisulphide of Carbon, CS_2.

12. 1st *Method.*

t	10°	55°	70°	75°	80°	85°	105°
x	2·4771	1·7183	1·6498	1·6206	1·6398	1·6515	1·8626

x has a minimum value 1·6206 at 75°. Hence

$$c - c_1 = 1\cdot6206 \times \frac{2}{76} = 0\cdot04265.$$

According to Hirn, at 80° $c = 0\cdot25531$; according to Regnault $c_1 = 0\cdot15956$; hence $c - c_1 = 0\cdot09575$. The latter figure is more than twice that found above—the difference is very considerable; nevertheless there can be no serious objection to such a discordance, for it has only to be admitted that there is an aggregate error of 0·05 in the specific heats, and the figures found for $c - c_1$ will both closely agree. Conversely, calculating c_1 from c and x we find that $c_1 = 0\cdot21266$ instead of 0·15956.

According to equation (9) we find

$$y = 3264\cdot26,$$

whence

$$r_0 = 3264\cdot26 \times \frac{2}{76} = 85\cdot901.$$

* See Notes at end.

According to Regnault it is 76·43. A certain disagreement proceeds from the fact that a considerable error might enter into the calculation of the amount of heat required to raise the temperature of the liquid from 0° to 85°, because Regnault's observations did not exceed 39°·5.

2nd Method.

t.	p.	$\dfrac{dp}{dt}$.	t.	p.	$\dfrac{dp}{dt}$.
60	1164·51		80	2032·53	53·127
65	1347·52		85	2311·70	
70	1552·09	43·182	90	2619·08	
75	1779·88	47·989			

t	70°		75°		80°
r	86·173		85·926		85·712
		0·211*		0·214	
$c - c_1$		0·0422		0·0428	

The mean value of $c - c_1$ 0·0425 and the value of r_0 85·926 do not differ from those found by the 1st method, 0·04265 and 85·901.

t.	Pressures.			t.	Pressures.		
	Calculated.	Observed.	Calculated from equation (5').		Calculated.	Observed.	Calculated from equation (5').
−20	47·96	47·30	47·99	90......	2618·5	2619·1	2618·9
0......	128·46	127·91		110......	4162·7	4164·1	
20......	298·31	298·03	297·38	130......	6296·8	6291·6	6306·5
40......	617·73	617·53		150......	9121·8	9095·9	9153·6
60......	1164·7	1164·5	1164·6				

* See Notes at end.

Carbon Tetrachloride, CCl_4.

13. 1st Method.

t	$-15°$	$-10°$	$-5°$	$0°$	$5°$	$10°$	$15°$	$20°$
x	5·2217	6·4753	6·2296	6·5014	5·8202	*6·8851*	6·0289	6·2210

t	$25°$	$30°$	$35°$	$40°$	$70°$	$75°$	$125°$
x	5·9630	5·9526	6·3706	5·5984	4·4596	4·2927	1·1511

The figures as we see proceed irregularly, but there is hardly any doubt that the maximum lies at $10°$.

$$c - c_1 = 6·8851 \times \frac{2}{154} = 0·08942 *.$$

It is impossible to compare this figure with the result of experiment, because the specific heat of the vapour of carbon tetrachloride is not known. But it is possible to conversely calculate this quantity, knowing $c - c_1$ and c. According to Regnault $c = 0·19979$, therefore $c_1 = 0·11037 *$.

By equation (9) we obtain

$$y = 4061·3,$$

whence

$$r_0 = 4061·3 \times \frac{2}{154} = 52·069.$$

According to Regnault $r_{10} = 51·45$.

2nd Method.

t.	p.	$\frac{dp}{dt}$.	t.	p.	$\frac{dp}{dt}$.
$-15°$	13·55		$15°$	71·73	3·4842
-10	18·47		20	90·99	4·2379
-5	24·83	1·4371	25	114·30	5·1070
0	32·95	1·8230	30	142·27	
5	43·19	2·2870	35	175·55	
10	55·97	2·8380			

t	$-5°$	$0°$	$5°$	$10°$	$15°$	$20°$	$25°$
r	53·295	52·865	52·467	52·063	51·654	51·264	50·870
		0·430	0·398	0·404	0·409	0·390	0·394
$c - c$		0·0860	0·0796	0·0808	0·0818	0·0780	0·0788

* See Notes at end.

The values of $c - c_1$ proved to be not quite similar to each other, or to the figure found by the 1st method, probably because the vapour-pressures, taken at rather low temperatures, are small and the errors they contain have a great influence on the calculation. The value of r_0, 52·063, however, is similar to the former value.

t.	Pressures.			t.	Pressures.		
	Calcu-lated.	Ob-served.			Calcu-lated.	Ob-served.	
-20......	9·76	9·80	9·79	40......	214·12	214·18	214·63
-10......	18·43	18·47	18·47	60......	442·87	447·43	445·61
0......	32·94	32·95	32·95	100......	1404·8	1467·1	1429·0
20......	90·97	90·99	91·00	140......	3316·9	3709·0	3421·1
30......	142·08	142·27	142·24	190......	7269·6	9399·0	7647·3

In order to verify the results, I repeated the calculations by the 1st method through intervals of 10°, between 10° and 40°.

t	$-10°$	$0°$	$10°$	$20°$	$30°$	$40°$
x	6·0955	6·2747	6·3953	6·1217	6·0431	5·6925

This table removes all doubt as to x attaining a maximum at 10°, hence

$$c - c_1 = 6·3953 \times \frac{2}{154} = 0·08305,$$

which is somewhat different from that found above, 0·08942. The same value is obtained for y as before, 4061·2. The vapour-pressures calculated from these data are given in the fourth column.

Ethylene Bromide, $C_2H_4Br_2$.

14. 1*st Method.*

In the case of ethylene bromide the calculations presented great irregularities, with which it was exceedingly difficult to deal. By means of numerous attempts and recalculations, I came to the conclusion that x has a minimum value of nearly zero, at 95°. The pressure at this point is equal to 245·51. Below this temperature, the errors contained in the vapour-pressures are probably considerable compared to the true

pressures, because the latter are small; owing to this the values obtained for x are irregular. But above $95°$ x increases regularly. If $x=0$ then $c=c_1$; unfortunately there are no direct experimental data for c_1. From equation (9),

$$y = 4606 \cdot 8,$$

whence

$$r_0 = 4606 \cdot 8 \times \frac{2}{188} = 49 \cdot 008.$$

According to Berthelot the heat of vaporization of ethylene bromide, under the atmospheric pressure, is equal to $43 \cdot 78$.

2nd Method.

The results obtained by this method also present a certain irregularity.

I here give several values.

t	$85°$	$90°$	$95°$	$100°$	$105°$
r	49·182	49·121	49·058	49·118	49·045
		0·061	0·063	−0·060	0·073
$c-c_1$		0·0122	0·0126	−0·0120	0·0146*

The difference $c-c_1$ is nearly zero, and the heat of vaporization $49 \cdot 058$ like that given above.

	Pressures.			Pressures.	
t.	Calculated.	Observed.	t.	Calculated.	Observed.
-20	0·85	1·73	80	144·24	144·02
-10	1·66	2·48	110	400·90	401·08
0	3·15	3·92	130	788·18	725·77
30	16·74	17·20	160	1607·7	1572·5
60	65·87	65·75	190	3203·2	5020·8

Methyl Alcohol, CH_4O.

15. 1*st Method*.

t	$-10°$	$15°$	$25°$	$30°$	$50°$	$70°$	$95°$
x	13·483	10·696	9·6978	6·4699	4·1952	3·3502	2·7869

t	$100°$	$105°$	$110°$	$115°$	$120°$
x	*2·7562*	2·8201	2·6484	2·8616	2·8190

Notwithstanding certain irregularities there can be no doubt but that x has a minimum value at $100°$.

* See Notes at end.

$$c - c_1 = 2\cdot7562 \times \frac{2}{32} = 0\cdot17226.$$

According to Kopp $c = 0\cdot645$, according to Regnault $c_1 = 0\cdot458$, $c - c_1 = 0\cdot187$, a result which is near to $0\cdot17226$. Conversely c_1 can be determined from the values of c and x; $c_1 = 0\cdot473$.

From equation (9) we have
$$y = 4356\cdot5$$
whence

$$r_0 = 4356\cdot5 \times \frac{2}{32} = 272\cdot28.$$

According to Andrews the value at $65\cdot8°$ is $263\cdot7$.

2nd Method.

t.	p.	$\frac{dp}{dt}$.	t.	p.	$\frac{dp}{dt}$.
$85°$	1470·92		$105°$	2806·27	85·292
90	1741·67		110	3259·60	96·194
95	2051·71	66·208	115	3769·80	
100	2405·15	75·309	120	4341·77	

t	$95°$	$100°$	$105°$	$110°$
r	273·13	272·28	271·42	270·56
		0·85	0·86	0·86
$c - c_1$......		0·170	0·172	0·172

The differences of the specific heats and the heat of vaporization determined by both methods are equal.

t.	Pressures.		t.	Pressures.	
	Calculated.	Observed.		Calculated.	Observed.
$-20°$	7·45	6·27	$60°$	580·65	579·93
0	28·73	26·82	80	1235·8	1238·5*
20	90·85	88·67	120	4342·8	4341·8
40	245·05	243·51	150	9369·2	9361·4

* The figure 8 is probably a misprint, it should be replaced by 5.

Acetone, C_3H_6O.

16. 1st *Method.*

t	$25°$	$30°$	$55°$	$60°$	$65°$
x	$3\cdot819$	$3\cdot426$	$2\cdot6888$	$2\cdot1175$	$2\cdot3053$

t	$70°$	$75°$	$80°$	$85°$	$90°$
x	$2\cdot2440$	$2\cdot4341$	$2\cdot4075$	$3\cdot1974$	$3\cdot1758$

t	$95°$	$125°$
x	$3\cdot3307$	$4\cdot7688$

Although there is an irregularity in this series of x's, still it is evident that x has a minimum value between $60°$ and $70°$; I take $65°$, and the arithmetical mean of three values of x answering to the temperatures $60°$, $65°$, and $70°$. In this manner I find

$$x = 2\cdot2227,$$

whence

$$c - c_1 = 2\cdot2227 \times \frac{2}{58} = 0\cdot076645.$$

According to Regnault $c = 0\cdot5580$ and $c_1 = 0\cdot4125$;

hence $$c - c_1 = 0\cdot1455.$$

Determining c_1 from c and x we find that $c_1 = 0\cdot4814$, and the difference between this value and that given by experiment, $0\cdot4125$, may be referred to errors in the calorimetric observations.

According to equation (9),

$$y = 3690\cdot37;$$

hence

$$r_0 = y \times \frac{2}{58} = 127\cdot25.$$

According to Regnault's formula, $r_{65} = 127\cdot54$.

2nd *Method.*

t.	p.	$\frac{dp}{dt}$.	t.	p.	$\frac{dp}{dt}$.
$50°$	$608\cdot86$		$70°$	$1189\cdot38$	$37\cdot264$
55	$725\cdot95$		75	$1387\cdot62$	
60	$860\cdot48$	$28\cdot774$	80	$1611\cdot05$	
65	$1014\cdot32$	$32\cdot825$			

t	$60°$		$65°$		$70°$
r	$127\cdot87$		$127\cdot48$		$127\cdot10$
		$0\cdot39$		$0\cdot38$	
$c - c_1$		$0\cdot078$		$0\cdot076$	

Both modes of calculation give similar results for $c - c_1$ and r_0.

t.	Pressures.			t.	Pressures.		
	Calcu-lated.	Ob-served.			Calcu-lated.	Ob-served.	
20	185·18	179·63	184·45	90......	2139·6	2141·7	2142·7
40	421·23	420·15	420·47	110......	3597·9	3594·0	3603·6
60	860·75	860·48	860·50	140......	7065·1	6974·4	7077·8
70	1189·0	1189·4	1189·4				

The irregularity in the sequence of the values of x caused me to recalculate them through intervals of 10°: I then obtained

t	50°	60°	70°	80°
x	3·0041	2·3514	2·2777	2·6131

Here it is quite clear that the minimum lies between 60° and 70°, and nearer to the latter temperature; I take the minimum as the arithmetical mean of 2·3514 and 2·2777, and refer it to 65°. In this manner it was found that

$$x = 2·3146;$$

$$c - c_1 = 2·3146 \times \frac{2}{58} = 0·07981.$$

I calculated y for two temperatures 60° and 70°, and took the arithmetical mean of the results.

$$y = 3696·6 ; \quad r_0 = 127·44.$$

I again calculated the vapour-pressures from these new values, the results are placed in the fourth column, they roughly satisfy the results of experiment as well as the figures in the second column do.

Chloroform, $CHCl_3$.

17. 1*st Method*.

t	25°	30°	60°	65°	70°
x	5·769	5·423	3·6488	3·3996	3·3502

t	75°	80°	85°	90°	100°	145°
x	3·3630	3·3510	3·4282	3·5686	3·630	5·117

x has a minimum at a temperature 70° to 80°, I take 75°, and the arithmetical mean of the three figures corresponding

to 70°, 75°, and 80° for x. We have
$$x = 3\cdot355,$$
$$c - c_1 = 3\cdot335 \times \frac{2}{119\cdot5} = 0\cdot05615.$$

According to Regnault $c = 0\cdot23894$, and according to Wiedemann $c_1 = 0\cdot1441$, hence $c - c_1 = 0\cdot0948$. If we assume that $c = 0\cdot23894$ and $c - c_1 = 0\cdot05615$, we find that $c_1 = 0\cdot18279$ instead of the value found by Wiedemann; both figures, taking calorimetric errors into consideration, may be counted as very similar. Furthermore we find

$$y = 3633\cdot1,$$
$$r_0 = 3633\cdot1 \times \frac{2}{119\cdot5} = 60\cdot805.$$

According to Regnault $r_{75} = 59\cdot602$.

2nd Method.

t.	p.	$\frac{dp}{dt}$.	t.	p.	$\frac{dp}{dt}$.
$6\overset{\circ}{0}$	755·44		$8\overset{\circ}{0}$	1407·64	40·935
65	889·72		85	1624·10	
70	1042·11	32·394	90	1865·22	
75	1214·20	36·492			

t	70°		75°		80°
r	61·207		60·916		60·648
		0·291		0·268	
$c - c_1$		0·058		0·054	

The mean of $c - c_1 = 0\cdot056$, $r_0 = 60\cdot916$. The same values are given above.

t.	Pressures.		t.	Pressures.	
$2\overset{\circ}{0}$	162·31	160·47	$10\overset{\circ}{0}$	2425·2	2428·5
50	536·06	535·05	130	4876·7	4885·1
70	1042·4	1042·1	165	9554·0	9527·8
80	1407·2	1407·6			

Ethyl Chloride, C_2H_5Cl.

18. 1st *Method*.

t	$-15°$	$-10°$	$-5°$	$0°$	$25°$
x	10·48	6·560	5·188	3·970	1·6209

t	$30°$	$35°$	$40°$	$45°$	$65°$
x	1·4039	*1·3183*	1·3334	1·3399	1·8691

The minimum of x lies at $35°$ and is equal to 1·3183: hence,

$$c - c_1 = 1·3183 \times \frac{2}{64·5} = 0·040878.$$

The specific heat c_1 is unknown. According to Regnault $c = 0·42760$; hence $c_1 = 0·38672$.

We then calculate y and r_0:

$$y = 3000·24,$$

$$r_0 = 3000·24 \times \frac{2}{64·5} = 93·032.$$

According to Regnault the heat of vaporization at the atmospheric pressure is 89·30.

2nd Method.

t.	p.	$\frac{dp}{dt}$.	t.	p.	$\frac{dp}{dt}$.
$20°$	996·23		$40°$	1919·58	58·656
25	1184·17		45	2230·71	
30	1398·99	45·820	50	2579·40	
35	1643·24	51·969			

t	$30°$	$35°$	$40°$
r	93·242	93·027	92·824
		0·215	0·203
$c - c_1$		0·0430	0·0406

The heats of vaporization determined by both methods were alike 93·027 and 93·032. The values for $c - c_1$ were also exceedingly near to each other.

$t.$	Pressures.		$t,$	Pressures.	
	Calculated.	Observed.		Calculated.	Observed.
$-20°$	192·39	187·55	$40°$	1919·6	1919·6
0	466·65	465·18	50	2579·5	2579·4
20	996·31	996·23	70	4407·4	4405·0
30	1399·0	1399·0	100	8771·3	8722·8

Ethyl Bromide, $C_2H_5Br.$

19. 1st *Method*.

t	$15°$	$25°$	$35°$	$45°$	$50°$
x	3·780	2·637	1·986	1·7282	1·5200

t	$55°$	$60°$	$65°$	$70°$	$75°$
x	1·4695	1·6066	1·6199	1·7383	1·7615

x has a minimum value at $55°$ which is equal to 1·4695. Hence

$$c - c_1 = 1·4695 \times \frac{2}{108·77} = 0·027017.$$

According to Regnault $c = 0·2153$, and according to Wiedemann $c_1 = 0·1744$; hence $c - c_1 = 0·0409.$

Conversely, assuming $c = 0·2153$ and $c - c_1 = 0·0270$, we find $c_1 = 0·1983$ instead of 0·1744 obtained by experiments. Further we have

$$y = 3296·47,$$
$$r_0 = 3296·47 \times \frac{2}{108·77} = 60·608.$$

According to Berthelot the heat of vaporization under the atmospheric pressure is 61·65; there do not exist any observations for other pressures.

2nd Method.

$t.$	$p.$	$\frac{dp}{dt}.$	$t.$	$p.$	$\frac{dp}{dt}.$
$40°$	801·92		$60°$	1511·92	44·843
45	947·28		65	1749·47	
50	1112·79	35·243	70	2015·06	
55	1300·35	39·848			

t	50°	55°	60°
r	60·752	60·616	60·470
		0·136	0·143
$c-c_1$		0·0272	0·0286

The arithmetical mean for $c-c_1$ will be 0·0279 and for r_0 60·616; both figures are similar to those given above by the 1st method.

t.	Pressures.		t.	Pressures.	
	Calculated.	Observed.		Calculated.	Observed.
-20	62·61	59·16	60	1511·9	1511·9
10	258·66	257·40	80	2639·4	2638·6
30	564·77	564·51	110	5414·5	5394·0
50	1112·8	1112·8	140	9923·4	9779·0

Ethyl Alcohol, C_2H_6O.

20. 1*st Method*.

t	75°	105°	120°	125°	130°
x	4·9002	6·7194	7·3370	7·7770	7·9890

t	135°	140°	145°	150°
x	7·9917	8·5192	8·6407	8·6754

The value of x gradually rises from a lower to a higher temperature. However, on examining the curve of x's it may be remarked that, notwithstanding its irregularity, it strives to attain a maximum, which lies about 150° or slightly higher. We assume that 150° corresponds to the maximum value of x, i. e. to 8·6754. Acting thus, we cannot naturally expect to obtain exact results. We shall have

$$c-c_1=8\cdot6754\times\frac{2}{46}=0\cdot3772.$$

According to Hirn $c_{150}=1\cdot0503$, and according to Regnault $c_1=0\cdot4797$; hence the experimental value of $c-c_1=0\cdot5706$. By equation (9) we find

$$y=4399\cdot9;$$

hence $r_0=191\cdot30$.

According to Regnault's formula it is 170·5.

2nd *Method.*

t.	p.	$\frac{dp}{dt}$.	t.	p.	$\frac{dp}{dt}$.
$135°$	4964·22		$150°$	7318·40	179·986
140	5674·59		155	8259·19	196·454
145	6458·0	164·259			

The differential coefficient $\left(\dfrac{dp}{dt}\right)$ 179·986, in the absence of

observations above 155°, was calculated by formula $\dfrac{dp_3}{dt}$ only,

and the differential coefficient 196·454 by formula $\dfrac{dp_4}{dt}$ only.

t	145°	150°	155°
r	193·22	191·33	189·44
		1·89	1·89
$c-c_1$	0·378	0·378	

The figures 0·378 and 191·33 do not differ from those found above.

t.	Pressures.		t.	Pressures.	
	Calculated.	Observed.		Calculated.	Observed.
$-20°$	1·71	3·34	$100°$	1689·4	1697·6
20	37·31	44·46	120	3229·8	3231·7
50	206·80	219·90	130	4322·4	4332·0
80	800·06	812·91	140	5674·3	5674·6

Sulphur.

21. 1st *Method.*

t	400°	480°	520°	540°	550°	560°
x	0·605	3·5244	4·4393	4·9409	*5·0616*	4·9683

x attains a maximum at 550°.

$$c-c_1 = 5·0616 \times \frac{2}{64} = 0·15817.$$

According to Personne, between 119° and 147°, $c = 0·2346$;

c_1 has not been measured, but it can be found from the preceding : $c_1 = 0.0764$.

From equation (9),

$$y = 7962,$$

hence

$$r_0 = 7962 \times \frac{2}{64} = 248.8.$$

According to Personne, at 316° the heat of vaporization of sulphur is 362.0. To render these data comparable they must be brought to one temperature. Being unable to do this accurately, we will calculate it approximately by subtracting the product of $0.15817 \times (550 - 316)$ from 362, which gives 37.0. Thus we have

$$r_{550} = 325.0.$$

2nd Method.

t.	p.	$\frac{dp}{dt}$.	t.	p.	$\frac{dp}{dt}$.
520°	2133.30		550°	3086.51	36.283
530	2421.97		560	3465.33	39.505
540	2739.21	33.203	570	3877.08	

The first two differential coefficients are the arithmetical means of two almost similar numbers; but the third coefficient, in the absence of data for the vapour-pressure at 580°, is a single value.

t	540°		550°		560°
r	250.37		248.82		247.09
		1.55		1.73	
$c - c_1$		0.155		0.173	

The arithmetical mean for $c - c_1$ is 0.164. Neither this value nor that of r_0 differ from those determined above.

t.	Pressures.		t.	Pressures.	
	Calculated.	Observed.		Calculated.	Observed.
390°	263.20	272.31	540°	2739.3	2739.2
450	774.59	779.89	560	3464.9	3465.3
500	1634.2	1635.3	570	3877.0	3877.1
530	2421.7	2422.0			

Mercury.

22. Mercury belongs to the small number of substances for which the maximum or minimum of x has a negative value. In this case $c-c_1$ must inevitably be < 0. Up to now, with all the substances investigated, it has been found that $c > c_1$. There is, however, no reason for affirming that this aspect of inequality is necessary; at least, in the mechanical theory of heat there is no indication one way or another. It is possible to imagine a substance which would at certain temperatures have a greater specific heat in a liquid than a gaseous state. The inequality $c < c_1$ induces the conclusion that the heat of vaporization increases with a rise of temperature when the vapour follows Boyle's and Gay-Lussac's laws. As a rule a converse phenomenon is observed, *i. e.* there is a decrease. Only ethyl alcohol, according to Regnault's experiments, offers a remarkable exception; the heat of vaporization increases as the temperature rises from 0° to 20°, and then follows the general law, *i. e.* it decreases. If x had a maximum or minimum value between 0° and 20°, then the inequality $c-c_1 < 0$ would be allowable between these temperatures.

1st Method.

t	250°	270°	280°	290°	300°
x	−2·9022	−1·8252	−5·2979	−4·8474	−4·6333

t	310°	320°	380°	430°
x	−4·5703	−2·6758	−3·4592	+0·1945

Although these figures present irregularities, still the minimum, without doubt, occurs between 280° and 300°. It may be said that the minimum value of x is equal to the arithmetical mean of its three values corresponding to temperatures 280°, 290°, and 300°, namely 4·9262, and lies opposite 290°. Hence

$$c - c_1 = -4 \cdot 9262 \times \frac{2}{200} = -0 \cdot 049262.$$

According to Kupffer, $c = 0 \cdot 0335$; c_1 has not been measured, but, on the basis of what has been said above,

$$c_1 = 0 \cdot 0335 + 0 \cdot 049262 = 0 \cdot 0828.$$

Further, we find

$$y = 7092 \cdot 6,$$
$$r_0 = 7092 \cdot 6 \times \frac{2}{200} = 70 \cdot 92.$$

According to Berthelot, r at the atmospheric pressure $= 70 \cdot 0$.

t.	p.	$\frac{dp}{dt}$.	t.	p.	$\frac{dp}{dt}$.
$260\overset{\circ}{}$	96·88*		$300\overset{\circ}{}$	242·15	5·2357
270	123·01		310	299·09	
280	155·17	3·5524	320	368·73	
290	194·46	4·3263			

* The tables give 73; if this value be left it gives certain irregularities. In my opinion it should be 88.

The last two figures of the differential coefficient contain errors.

t	280°	290°	300°
r	70·010	70·520	70·990
		−0·516	−0·470
$c-c_1$		−0·0516	−0·0470

The arithmetical mean for $c-c_1$ is equal to $-0\cdot0493$; and $r_0 = 70\cdot52$. Both values are equal to those which were obtained by the first method. Besides which we see that here the heat of vaporization increases with a rise of temperature, and that the quantity $c-c_1$ has a negative value, as was found by the other method.

t.	Pressures.		t.	Pressures.	
	Calculated.	Observed.		Calculated.	Observed.
$0\overset{\circ}{}$	0·002	0·020	$300\overset{\circ}{}$	242·44	242·15
80	0·203	0·353	320	370·19	368·73
160	5·33	5·90	360	809·00	797·74
220	34·20	34·70	420	2281·8	2177·5
280	154·96	155·17	520	9734·2	8265·0

23. The vapour-pressures of the acids $C_nH_{2n}O_2$, formic, acetic, propionic, butyric, and isovaleric, were measured by Landolt, but unfortunately with considerable errors. Thus, in the case of propionic acid, he gives a vapour-pressure 389·0 for 120° and 650·2 for 135°, both of which figures are, without doubt, wrong. It is scarcely possible to deal with these

mistakes and correct the errors, rough as they may be, proceeding perhaps from misprints and mistakes in interpolation. It is exceedingly remarkable that with the majority of acids x has a negative value. Whether $c - c_1$ is negative depends upon x being so when it attains a maximum or minimum value. Acetic acid apparently offers less error, and I here insert my endeavours to bring our theory into agreement with Landolt's data for this acid.

Acetic Acid, $C_2H_4O_2$.

1st Method.

In order to shorten the calculations, I calculated the numerator of equation (8). Its different values are placed in the second line of the following table; the first line contains the corresponding temperatures:—

t	$50°$	$55°$	$60°$	$65°$	$70°$	$75°$
x	0·225	0·405	0·417	0·329	0·206	0·303

t	$80°$	$85°$	$90°$	$95°$	$100°$	$105°$	$110°$
x	0·428	0·203	0·405	0·132	0·325	0·106	0·309

On dividing these figures by the denominator of equation (8), which is always negative, we find that all the x's are also negative. x increases with a rise of temperature above $110°$ and a fall below $50°$, hence its maximum value lies between these temperatures; but it is impossible to indicate the exact corresponding temperature, owing to the disorder of the figures. I take $80°$, because in the preceding table the maximum quantity lies opposite it. To determine as accurately as possible the minimum of x, it is necessary to divide the figures of the second line by the corresponding numerators and to take the arithmetical mean of the thirteen figures so obtained. As the latter are too irregular it is impossible to expect a great accuracy from the mean result; I therefore changed this method for another, which, although less accurate, is simpler, counting that this would not render the calculations less exact. I took the arithmetical mean of the figures of the second line of the preceding table and divided the number so obtained, 0·2848, by the numerator of equation (8) taken for the temperature $80°$. I found

$$x = -9·2657,$$

whence

$$c - c_1 = -9·2657 \times \frac{2}{60} = -0·30886.$$

According to Regnault, $c = 0·4599$ (between $10°$ and $15°$); c_1 is unknown. From these data we find

$$c_1 = 0·7688.$$

G 2

I calculated y for three temperatures, 75°, 80°, and 85°, taking the value of x the same in each case $-9\cdot2657$, and took the mean of the results.   I found

$$y = 4205\cdot3,$$

$$r_0 = 4205\cdot3 \times \frac{2}{60} = 140\cdot2.$$

According to Berthelot, the heat of vaporization under the ordinary pressure (175°?) is 120·1.

2nd Method.

t.	p.	$\frac{dp}{dt}$.	t.	p.	$\frac{dp}{dt}$.
60°	97·4		85°	244·1	8·597
65	117·8		90	290·6	10·077
70	142·0		95	345·2	
75	170·6	5·260	100	408·5	
80	204·3	7·324			

Each $\frac{dp}{dt}$ is the arithmetical mean of two figures which do not agree very well together owing to the errors contained in the pressures.   Thus the differential coefficient for the pressure 244·1 calculated as $\frac{dp_3}{dt}$ from pressures 170·6, 204·3, 244·1, and 290·6 proved equal to 8·611 ; and that calculated after the formula $\frac{dp_2}{dt}$ from pressures 204·3, 244·1, 290·6, and 345·2 equalled 8·583.   Hence in the mean 8·597 an error may be suspected in the two last ciphers ; which error should also enter into the figure expressing the heat of vaporization.

t	70°	75°	80°	85°	90°
r	145·27	146·76	148·91	150·46	152·31
		$-1\cdot69$	$-2\cdot15$	$-1\cdot55$	$-1\cdot85$	
$c-c_1$		$-0\cdot338$	$-0\cdot430$	$-0\cdot310$	$-0\cdot370$

The values of $c-c_1$ and of r_0 found by the two methods differ considerably.   This indicates, as has been already said, the insufficient accuracy of the observations on the vapour-pressure of acetic acid.

$t.$	Pressures.			$t.$	Pressures.		
	Calculated.	Observed.			Calculated.	Observed.	
$\overset{\circ}{0}$	8·7	7·6	9·0	$\overset{\circ}{70}$	144·9	142·0	139·0
20	21·1	18·9	20·9	90	284·8	290·6	274·6
40	47·8	44·1	42·2	100	392·4	408·5	380·6
50	...	66·0	67·5	120	723·3	781·1	712·6
60	101·5	97·4	97·4	140	1285·5	1931·3	1293·5

Finding the preceding calculations of the value of x unsatisfactory, I repeated them at intervals of $10°$.

t ...	$50°$	$60°$	$70°$	$80°$	$90°$	$100°$
x ...	-10.984	-12.005	-9.8238	-11.094	-9.5669	-9.3295

There is still an irregularity, but the position of the minimum is clearer, it is equal to $12·005$ and lies opposite $60°$. Hence

$$c - c_1 = 0.4002.$$

We then find

$$y = 4022·2 ; \quad r_0 = 130·7.$$

I calculated the vapour-pressures of acetic acid from the new values of x and y, and placed them in the fourth column of the preceding table.

24. There are some liquids to which our theory cannot be applied, at least at present, owing to the insufficiency of observations on their vapour-pressures in a state of saturation. Among these are:—

$$C_2H_5I, \ PCl_3, \ BCl_3, \ SiCl_4, \ CNCl_2, \ C_2H_4Cl_2, \ \text{and} \ C_{10}H_{16}.$$

With the first five liquids x increases with a rise of temperature, but with the last two x decreases. If the curve of x's be constructed, it is easy to observe that it strives to attain a maximum or minimum, and with the first six liquids it probably does so not far beyond the highest temperature at which observations were made. In the case of turpentine this temperature lies far beyond the temperatures observed.

25. I have, as far as I know, reviewed all the liquids whose vapour-pressures have been well determined ; there remain the liquids produced by the liquefaction of gases under high pressures. Our theory should not, however, be applied to them, chiefly because the volume of the liquid presents a

considerable magnitude compared to that of the gas in a state of saturation. The application of this theory to such liquids is, however, interesting, because it enables us to calculate their heat of vaporization, the determination of which by experiment is very difficult. For this reason I allowed myself to apply the theory to certain gases, although it was impossible to expect reliable results. It appeared that the existing experimental data on liquefied gases in a state of saturation were exceedingly rough, and did not permit making any even approximately exact conclusions. Besides which certain gases give a constant increase of rate of decrease on the value of x with a rise of temperature. Only sulphuretted hydrogen (H_2S) gave the possibility of obtaining x and y, although only very approximatively. I here give the results only, without the calculations. The temperature of the maximum was 65°.

$$x = 3\cdot3987, \; y = 2045\cdot3,$$
$$c - c_1 = 0\cdot2000, \; r_0 = \;120\cdot3.$$

I calculated the vapour-pressure of sulphuretted hydrogen in a state of saturation, at various temperatures, from these data.

$t.$	Pressures.		$t.$	Pressures.	
	Calculated.	Observed.		Calculated.	Observed.
-20	4135·0	4438·5	50......	27809	27815
0	8051·6	8206·3	60......	33740	33740
20	14071	14152	70......	40352	40353
40	22563	22582			

26. The second mode of determining the value of x and the latent heat of vaporization requires an exact knowledge of the differential coefficient of the pressure $\left(\dfrac{dp}{dt}\right)$. This quantity may, as was shown above, be calculated from four different formulæ (11): I only determined two values in each instance. If the latter were equal, within the limits of logarithmic errors, then the results of observation might be relied upon: in the reverse case the data for the pressures contained errors, made by the composers of the tables, in their calculations of the interpolation formulæ, or else due to misprints. The

unreliability of the data may also be remarked in calculating
x after the first method; it evinces itself in the irregularity
of the resultant values. But it is somewhat difficult to deter-
mine the extent and locality of the errors: to do this it is
necessary to compose a table of the differences of different
series of data for the pressures; if there are errors, irregu-
larities then appear in the second or third of the differences.
Such are, for example, the vapour-pressure of ether at 40°,
907·04 (Regnault, vol. xxvi. p. 393); of bisulphide of carbon
at 95°, 2966·34 (p. 402); of propionic acid at 120°, 389·0, and
at 135°, 650·2 (Landolt's Tables, p. 55). All these data are
erroneous, but I have not been able to determine the extent
of the error. The vapour-pressure of methyl alcohol at 80°,
given as 1238·47 (Regnault, vol. xxvi. p. 460), should be
1235·47. The vapour-pressure of acetone at 50°, 602·86
(p. 472), should be 608·86; of mercury at 380° (p. 521),
1139·65 should be 1136·65; at 260° it should be 96·88 and
not 96·73. The value 5072·43 at 480° is also very doubtful.
In Landolt's Tables (p. 57) the vapour-pressure of benzene,
given as 5683·03 should be 5789·03. This misprint is, how-
ever, mentioned by Regnault, but is inserted in his tables
without correction. Lastly, in Regnault's tables (vol. xxi.)
of the vapour-pressure of steam, there are several errors which
have been reprinted without correction in many works.

Conclusion.—The pressure of a vapour in a state of satura-
tion is expressed by equation (5). The values of $c-c_1$ and of
r_0 may be taken from experimental data, but are better calcu-
lated, looking upon them as arbitrary constants, from tables
of vapour-pressures, because the latter can be determined from
experiment with far greater accuracy than the former. How-
ever, the values obtained for r_0 by either method differ but
slightly, with the exception of those cases when considerable
errors may be suspected in the values of the vapour-pressures
or r_0 determined by calorimetric measurements. The values
obtained for $c-c_1$ differ far more. This is due, as has been
already explained, to the fact that even slight errors in c and
c_1 produce an immense effect upon the value of $c-c_1$. If we
carefully follow out Regnault's method for measuring c_1, we
inevitably come to the conclusion that the specific heat of a
vapour may contain a very large error, because it is calculated
from the difference between two quantities of heat which are
exceedingly great compared to the magnitude of their differ-
ence. Consequently, the error in $c-c_1$ may be so great that

it is impossible, in my opinion, to make any true conclusion from the magnitude of $c-c_1$.

If the temperature T_0 be determined with sufficient accuracy, then both methods used for calculating it give one and the same result, just as they do for r_0 and $c-c_1$. If, on the contrary, we purposely take an incorrect, but more or less likely value for T_0, then it gives dissimilar results. This shows that the above enunciated theory has a firm basis and gives a right to hope that the values found for r_0 and $c-c_1$ deserve greater confidence than those given by calorimetric methods.

It would be very important in relation to the confirmation of our proposed theory to prove experimentally or theoretically the truth of its fundamental proposition—that vapours in a state of saturation subject themselves to Boyle's and Gay-Lussac's laws. The only existing means of doing this, namely the formula

$$v-w = \frac{1}{A} \cdot \frac{r}{T\dfrac{dp}{dt}},$$

cannot, however, be made use of, because the quantity r cannot be considered as determined with sufficient accuracy by experiment. Besides which this quantity has been measured at different pressures for only a very few liquids; in the case of a very few of which is it possible to calculate w owing to the coefficients of expansion being unknown at high pressures. I applied the preceding formula to aqueous vapour, and made use of Zeuner's Tables, in which the value of $A(v-w)p$ is given for various temperatures: I added Awp corresponding to the same temperatures, and divided the sum by AT. The figures thus obtained present the expression

$$\frac{pv}{T},$$

which, with a small variation of temperature ($20°-40°$) on either side of T_0, should not vary within the limits of experimental errors. Unfortunately, the figures so obtained were so irregular that it was impossible to come to any rational conclusion from them.

At temperatures remote from T_0 the results given by equation (5) sometimes differ from the data given in tables. From this it should in no way be concluded that the bases of this formula are false. It only indicates that the vapour under consideration diverges on one side or another from the laws of Boyle and Gay-Lussac at temperatures remote from T_0. Some vapours preserve the properties of a perfect gas

for large amplitude of temperature, others do not. Among the former are, sulphur (390° to 570°), sulphide of carbon (−20° to 130°), water (−30° to 100°) benzene (40° to 170°), ether (0° to 110°) and others, while the latter include carbon tetrachloride, ethene bromide, methyl alcohol, and others.

Yalta, January 1891.

Note on Prof. Kraevitch's *Paper.   By* Prof. Geo. Fras. FitzGerald.

It may be worth while pointing out in connexion with this paper that the author seems to attribute too much importance to the fact that his two methods of calculating the specific and latent heats agree.   His second method consists in calculating the latent heat of vaporization r from the thermodynamic formula

$$r = A(v - w)T \cdot \frac{dp}{dT},$$

and then using this value in his own formula

$$r = r_0 - (c - c_1)(T - T_0).$$

His first method consists in substituting r out of the second of these equations in the first and then integrating through the small range of temperature T to T_0. In both cases, for reasons he gives he assumes that the vapour obeys Boyle's and Dalton's laws, and that $c - c_1$ is constant throughout the ranges of temperature employed. This he does explicitly in his first method, but these assumptions are equally necessary for his second method, for the first of these equations, as used by him, is modified by an assumption of the validity of Boyle's and Dalton's laws, and the second is explicitly derived from a differential equation by assuming $c - c_1$ constant within the limits of integration, and these limits are mostly the same as those he subsequently employs to obtain the equation he uses in his first method.   Hence the two methods are not independent, and the fact that they do not lead to exactly equal numerical results is largely due to the difficulty he takes so much trouble to surmount of calculating $\frac{dp}{dt}$ at the temperature required.   There are in addition several arithmetical mistakes which would require laborious calculations to correct, as some of them may be mistakes in the elaborate calculations which are not given fully in the paper.

Note by Prof. WILLIAM RAMSAY.

This paper reached my hands from Professor Mendeléeff with the request that it should be published in the Philosophical Magazine. Professor FitzGerald has had the kindness to see it through the press, and has made some alterations which were necessary from thermodynamical considerations. It is unfortunate that Professor Kraevitch has made use of data in verifying his equations which are, to say the least, not the best attainable. But the main fact, that he has devised a rational formula which makes possible the calculation of vapour-pressures, by means of data derived from other physical constants, is of great importance.

V. *The Action of Electromagnetic Radiations on Films containing Metallic Powders.* *By* Professor G. M. MINCHIN, *M.A.*[*]

AT the last Edinburgh meeting of the British Association attention was directed by Dr. Dawson Turner to a discovery made by M. E. Branly, as to the effect produced on a glass tube filled with copper filings through the extremities of which tube are inserted two wires which dip into the filings (without, of course, touching each other inside the tube). The filings form, apparently, a continuous column of metal, the tube when held up to the light being opaque. Supporting the tube in a horizontal, or any other, position, and connecting its terminal wires with a galvanometer and a voltaic cell in a continuous circuit, the chances are that no current whatever will be indicated by the galvanometer. If such a current happens to exist, a very slight tap given to the tube or to its support will destroy the conductivity of the column of filings, and no current passes. Another such tap will cause the column to conduct, and so on.

At first sight it seems strange that such a metallic column should be a non-conductor ; but, of course, when we see the result we can admit that the contact between every particle and its neighbours is of the microphonic kind, and thus that the whole column may be an extremely bad conductor.

The identity of the state of affairs in the tube with that in a microphone may be perceived by inserting a telephone in the circuit, and then we shall find that slight mechanical disturbances communicated to the column of filings will be

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accompanied by the rumbling noises which are heard in a telephonic circuit which contains a microphone.

Now the most striking peculiarity of such a column is that, while it is in the non-conducting state, if a spark is allowed to pass anywhere in its neighbourhood between the knobs of a Leyden jar or the poles of an induction-coil, the waves sent out from the spark at once render the column a conductor.

This experiment was reproduced at the meeting of the Physical Society on October 27 by Mr. Croft, and it at once struck me as bearing a strong resemblance to the effects produced by electromagnetic waves on photoelectric impulsion-cells. These cells I have already fully described (see ' Philosophical Magazine,' March 1891) ; and in addition to what I showed with regard to them, I may here add that the effects of the sparks of an induction-coil on an impulsion-cell were observed when the cell (enclosed in a dark box) was over 140 feet distant from the coil and from everything connected with it. Moreover, it was found that, *in most cases*, the power of electromagnetic radiations to change the state of the cell from one of insensitiveness to one of sensitiveness to light depends on the length of the electromagnetic waves ; for, by adding capacity (by means of Leyden jars) to the sparking circuit, the waves ceased to affect the cell, and, on removing this capacity, their ability to effect the change was restored.

I have always held that this action of the cell is due to a rearrangement of the molecules on the sensitized surface of the plate in the cell by the electrical disturbances produced in the wires connected with its poles, these disturbances being due to the radiations emanating from the sparking circuit ; and I found that by completely enclosing the cell, *together with its terminal wires,* in a metal box, the ability of the radiations to act on the cell was destroyed.

After having seen the experiment shown by Mr. Croft, I filled several glass tubes with the filings of copper, tin, zinc, bismuth, antimony, &c., and found M. Branly's result in every case. It seems to me that if the filings are extremely fine (powders, in fact) the result is much more difficult to obtain. Powders used in this way are very great insulators, and they must be strongly pressed together by the corks which close the glass tubes in order to conduct ; but then it becomes difficult to alter their conductivity by mechanical disturbances. On the other hand, a tube filled with very coarse iron filings was found to conduct under all circumstances ; so that, apparently, the filings must be neither very fine nor very coarse.

As in the case of the impulsion-cells, the effect of the electromagnetic disturbances is cut off by completely enclosing the tubes and their terminal wires in a metal box. If the terminal wires are allowed to project outside the box—whether they are connected with the battery and galvanometer or not—the tubes are affected, which clearly shows that the result is due to the electrical disturbances set up in the leading wires of the tube.

In order to establish a closer connexion with the impulsion-cells, it seemed to me that films containing metallic particles almost in mathematical contact, but yet free to undergo very minute displacements of rotation, should replace the tubes of filings. Accordingly, I have formed such films by imbedding fine metallic powders in layers of gelatine and of collodion. The powders which I employ in these films are very much finer than the filings which I have used in the glass tubes.

The media, or bases, in which these powders are embedded are (so far as I have gone) gelatine and collodion.

To form a gelatine film proceed thus :—Pour a very thin layer of dissolved gelatine over a glass or ebonite plate ; let this layer get almost quite dry : if it gets quite dry, hold it over a beaker of boiling water until it absorbs a sufficient quantity of steam to render it very slightly plastic : take a test-tube with fine metallic powder immersed in alcohol ; shake this up well, and rapidly pour some of it over the gelatine surface, securing, to all appearance, both continuity and uniformity of the metallic layer. The alcohol soon evaporates, leaving the metallic layer embedded in the gelatine, but not wholly sunk below it.

In the case of a collodion film, the metallic powder is shaken up in a test-tube and then rapidly poured over a glass plate. After some time the film dries and peels off the plate. The surface of the film which was in contact with the glass is the metallic surface sought ; the other surface of the film probably contains no metallic particles, and is simply a continuous surface of dry collodion which is an absolute non-conductor.

If the layer of gelatine above described is too thick, it will probably happen that its upper surface (that remote from the glass or ebonite plate) does not contain metallic particles, and is a non-conductor. In this case, if the film is peeled off the plate there remains on the plate a metallic surface which will answer our purpose.

Such a film may now replace the tube of filings in M. Branly's experiment.

Let ABCD represent the film, L a battery of one or two voltaic cells, G a galvanometer, and K a key which can be connected with the film by means of the wires *s, w,* the
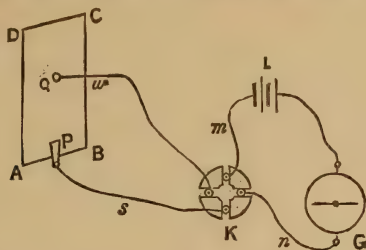
former clamped to the film at a point P, while the latter ends in a stout platinum piece the end of which is a round knob touching the film at a movable point Q.

Now it is found that when the contacts are all made no current passes, and we have to begin by making the platinum knob touch the film very close to P—perhaps $\frac{1}{2}$ millim. from P. Still no current passes, even when a spark of an induction-coil is allowed to pass a few feet from the film. But by touching either of the wires *s, w* with an electrified body (that which I commonly use is a common gas-lighting electrical machine), the resistance of the film and the contacts P, Q is overcome, and a strong current is shown by the galvanometer. We can now gradually increase the distance between P and Q each time that Q is removed from P, the wire *s* or *w* being touched by the electrified body ; and by these successive steps the whole of the film is finally rendered conducting.

The special characteristic of such a film which I wish to point out is this : if, while the film is conducting, the current is stopped by breaking the contact at Q, the film will be found to be a non-conductor if the contact is almost instantly re-made at the same point Q ; while, if the contact is broken anywhere else in the circuit, as at K, and then re-made, the film will still be found to conduct.

Again, if when the film has been rendered a conductor, the circuit is broken at K, and left broken for (apparently) any length of time, and then re-made, the film will be found to be still a conductor.

The breaking of the contact at Q is instantly fatal to the conductivity of the film, if the film is not many days old ; but, after some days, it will be found that on breaking the contact at Q and then re-making it, the film remains a conductor, unless we delay the re-making of the contact for half

a minute or so.   Doubtless this is due to the fact that, as the film gets more hard and less plastic, the metallic particles find it more difficult to move, by rotation or otherwise, in their environment.

Finally, these films are very much less sensitive to mechanical disturbances given to their supports than the tubes of filings.   They do not appear to be susceptible to the action of heat ; but in many instances their conductivity was destroyed by breathing upon them, or by allowing a stream of steam to strike their surfaces, the conductivity being always restored by the electromagnetic radiations.   The more rapid vibrations of light have not produced any effect so far as my observations have gone.

The prime cause of the action is to be sought in the electrical surgings produced in the leads s and w ; but it is clear that the state of affairs at the places P, Q of contact of the film with the electrodes is a most important matter.

It seems clear, therefore, that the sensitized surface in an impulsion-cell has a close analogue in a slightly plastic film filled with almost mathematical completeness by fine metallic particles.

VI. *On the Sudden Acquisition of Conducting-Power by a Series of Discrete Metallic Particles.   By* Prof. OLIVER J. LODGE [*].

THE recent experiments of Mr. Croft and Prof. Minchin remind me of an observation I frequently made when engaged with the syntonic arrangement of Leyden-jar circuits, or sympathetic electric resonance.   I found, if the knobs of the receiver were very close together, a weak battery and bell being in circuit, that the occurrence of a scintilla at the receiver frequently caused the bell to ring for some time, and in general to show signs that the knobs were in a state of feebly adhesive contact.   It was just as if their surface-layers or skins had been broken through, or opened out, in such a manner as to increase the molecular range of a few of the closest superficial molecules and thereby to cause cohesion to set in at a distance considerably greater than the ordinary distance.

A phenomenon which may be similarly caused is that discovered by Lord Rayleigh, with regard to the effect of electrified sealing-wax near a vertical water-jet : drops which would otherwise have rebounded being thereby caused to cohere. And, by the method of two impinging jets, the necessary

difference of potential was shown to be only a volt or two, since a pair of impinging jets ceased to rebound if connected to the opposite terminals of a Grove cell.

Once more, the effect first observed by Mr. Guitard (1850), and rediscovered by myself and the late J. W. Clark, concerning the adhesion of dust-particles or mist-globules in electrified air, is but a more violent variety of the same sort of effect. And the action of electricity on a steam-jet discovered by Robert von Helmholtz and afterwards by Shelford Bidwell, and worked at by Richarz, Aitken, J. J. Thomson, and others, may not be very different.

Thinking of the Lord Rayleigh variety of experiment as in many respects the most definite, it is natural to explain it electrolytically as due to the polarisation of the water-drops, or the formation in each drop of molecular chains each with a negatively charged oxygen atom at its termination on one hemisphere and a positively charged hydrogen atom at its opposite extremity.

Such drops then colliding about the region of their poles would be attracted not only by their ordinary cohesive forces, but by electrical force also, and thus the effective molecular range would be increased and cohesion might set in over an unusual distance.

In some such way I have allowed myself to fancy that the adhesion of my knobs might be explained, and I suggest that the conductivity of a chain of metallic filings under an electric polarising influence may be due to something of the same cause.

That a tap should break the minute points of contact is likely enough, though I see no reason why another tap should restore communication,—if so it does.

At the last moment I write this and send it off in the hope that it may arrive in time to be read at the Meeting as a contribution to the discussion on these interesting experiments.

Nov. 23, 1893.

VII. *On the Magnetic Shielding of Concentric Spherical Shells. By* A. W. Rücker, *F.R.S.*[*]

SPECIAL interest has of late attached to the problem of shielding magnetic forces by means of iron screens, and recently the Astronomer Royal has described the arrangement (designed by Messrs. Johnson and Phillips) by which

he has protected the absolute magnetic instruments at Green-wich from the disturbances due to a dynamo.

In that case external space was protected against magnetic forces produced inside the enclosure.

The converse arrangement is sometimes adopted, and, as in Lord Kelvin's Marine Galvanometer, instruments are enclosed in iron and thus protected against external mag-netic influence.

In the particular case when the iron shields are spherical shells, the method of attacking the mathematical problem involved is well known. Maxwell gives the working in the case of an internal space protected by a single shell (Ed. 3, vol. ii. p. 59), and also discusses the precisely analogous problem of the flow of currents interrupted by shells of dif-ferent conductivity from the rest.

I believe, however, that a number of facts, which are of some practical importance, are not generally known, and I propose therefore to deal with them in the following paper, illustrating them by numerical examples.

In the earlier part of the paper the general theory is developed, chiefly for the sake of defining the notation used, though this course involves some recapitulation from Maxwell. The discussion of the best conditions for shielding, with which I mainly deal, is, I believe, new.

The principal point to which attention is directed is the calculation of the advantage gained by lamination, *i. e.* by using shields separated by air-gaps, like those employed by Mr. Christie, instead of a continuous mass of iron.

That lamination would be useful might be foreseen by the aid of the hydrodynamical analogue to the magnetic field.

If we suppose sources and sinks of equal power to be placed within an enclosure, we may weaken the flow outside, either by making the enclosure or part of it very permeable, or by making the bounding surface very impermeable.

In like manner in the magnetic problem there are two ways of reducing the internal field, viz. by enclosing the central region by shells of greater, or by shells of less, permeability than the surrounding space. Although we cannot in practice use any material of less permeability than the air, we can introduce into an iron shell layers of material less permeable than itself. These may tend to reduce the external field by preventing as it were the force from penetrating to the external shell.

This analogy has long suggested that laminated shells, in which both the permeability of the iron and the relative impermeability of other materials are utilized, may be the

most effective shields; and we are thus led to enquire which is the best arrangement that can be made under specified conditions as to the magnitude of the space at our disposal or as to the weight of the shielding material used. The answer to this question is supplied by the following discussion.

As the formulæ are somewhat heavy, I shall for the most part confine myself to shells formed of the same material and separated by air-gaps.

The second problem, to the result of which I think it is desirable to draw attention, is that which defines the relations between the shielding exerted by a number of concentric shells, (1) on external space when the magnetic forces are produced within the shells ; and (2) on the enclosed space when the magnetic forces are produced outside. A full discussion of this is given below.

The whole of the investigation is subject to three limitations. I have confined myself:—

(1) to concentric shells ;
(2) to cases in which the equipotential surfaces are surfaces of revolution about a line through the common centre of the shells ;
(3) to the case in which the permeability of each shell is constant.

As regards the first two limitations, I think it will be seen that the conclusions arrived at are capable of generalization in such a way as to enable a better approach to be made to good shielding arrangements than would be the case if the results of the discussion in the simple case of spherical shells were unknown. The third limitation no doubt affects the applicability of the formulæ to practice. In spite of this, however, I venture to think that they afford some useful guidance, and that at all events they help to put the practical problem in definite terms.

The Relation between the Shielded and Unshielded Fields when the Shielded Space is (1) *within,* (2) *without the Shielding Shells.*

Take the common centre of the shells as origin. Let the potential within any shell be expanded in terms of zonal spherical harmonics, then the terms corresponding to P_n will be of the form

$$\left(A_n r^n + \frac{B_n}{r^{n+1}}\right)P_n.$$

Each such term can be discussed independently, and it is

more convenient to make the subscript numbers refer to the shell than to the order of the harmonic.

If, therefore, there are m shells, let the radii of the surfaces of separation be a_0, a_1, a_2, &c. a_m. Then a_0 is the radius of the central space, a_1, a_2, &c. are the external radii of consecutive shells (see figure).
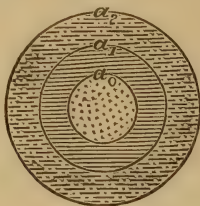
Let μ_0, μ_1, ... μ_m be the permeabilities of the enclosed space and of the shells, and for generality let M be the permeability of external space.

Let the coefficient of P_n in the expansion of the potential in the pth shell be

$$\phi_p r^n + \psi_p/r^{n+1}.$$

Then at the boundary between the pth and the $(p+1)$th shells (of which the radius is a_p) the following conditions must be fulfilled:—

$$\phi_p a_p^n + \psi_p/a_p^{n+1} = \phi_{p+1} a_p^n + \psi_{p+1}/a_p^{n+1},$$

and

$$\mu_p\{n\phi_p a_p^{n-1} - (n+1)\psi_p/a_p^{n+2}\}$$
$$= \mu_{p+1}\{n\phi_{p+1} a_p^{n-1} - (n+1)\psi_{p+1}/a_p^{n+2}\};$$

or if we write

$$N = (n+1)/n, \qquad \alpha_p = a_p^{-(2n+1)},$$

we get

$$\phi_p + \psi_p\alpha_p - \phi_{p+1} - \psi_{p+1}\alpha_p = 0,$$

and

$$\mu_p\phi_p - N\mu_p\alpha_p\psi_p - \mu_{p+1}\phi_{p+1} + N\mu_{p+1}\alpha_p\psi_{p+1} = 0.$$

If we suppose, for the sake of symmetry, and without reference for the moment to the expression of physical facts, that the coefficients of P_n in the potentials in the central enclosed space and in external space are

$$\phi_0 r + \psi_0/r^{n+1} \quad \text{and} \quad \Phi r^n + \Psi/r^{n+1}$$

respectively, we have in all $2m+4$ quantities to deal with, and since the m shells have $m+1$ bounding surfaces, there

are $2m + 2$ equations between them, all of which are linear and of the types given above.

We thus get a series of equations as follows :—

$$
\left.
\begin{aligned}
&\Phi + \Psi\alpha_m - \phi_m - \psi_m\alpha_m = 0. \\
&\mathrm{M}\Phi - \mathrm{MN}\Psi\alpha_m - \mu_m\phi_m + \mu_m\mathrm{N}\psi_m\alpha_m = 0. \\
&\phi_m + \psi_m\alpha_{m-1} - \phi_{m-1} - \psi_{m-1}\alpha_{m-1} = 0. \\
&\mu_m\phi_m - \mu_m\mathrm{N}\psi_m\alpha_{m-1} - \mu_{m-1}\phi_{m-1} + \mu_{m-1}\mathrm{N}\psi_{m-1}\alpha_{m-1} = 0. \\
&\qquad\text{\&c.,} \qquad\qquad\qquad \text{\&c.} \\
&\phi_2 + \psi_2\alpha_1 - \phi_1 - \psi_1\alpha_1 = 0. \\
&\mu_2\phi_2 - \mu_2\mathrm{N}\psi_2\alpha_1 - \mu_1\phi_1 + \mu_1\mathrm{N}\psi_1\alpha_1 = 0. \\
&\phi_1 + \psi_1\alpha_0 - \phi_0 - \psi_0\alpha_0 = 0. \\
&\mu_1\phi_1 - \mu_1\mathrm{N}\psi_1\alpha_0 - \mu_0\phi_0 + \mu_0\mathrm{N}\psi_0\alpha_0 = 0.
\end{aligned}
\right\} (1)
$$

In the case of shielding an enclosed space the potential of the inducing forces can be expanded within and in the neighbourhood of the shells in terms of positive powers of r, and since the potential of the induced magnetization must be finite when $r = 0$, this also is included in ϕ_0. Hence $\psi_0 = 0$. In external space the expansion of the potential contains both positive and negative terms, the former due to the inducing, and the latter to the induced magnetization.

As the inducing forces are given Φ is known.

As $\psi_0 = 0$ and Φ is given, the number of unknowns is reduced by 2 and is equal to the number of the equations.

If, on the other hand, the inducing forces are produced in the central space within the shell, their potential must be expanded in inverse powers of r if the series is to be convergent at the boundary of the enclosure and beyond it. Hence ψ_0 is known. In external space the terms due both to the induced and inducing magnetizations are expressed in negative powers, and are included in Ψ. Thus $\Phi = 0$.

Now ϕ_0/Φ is the ratio of the shielded to the unshielded field in the first case, in so far as it depends on the potential term under consideration, and Ψ/ψ_0 is the corresponding quantity when the forces are produced within the shell.

The relation between these may now be found.

Putting $\psi_0 = 0$ and writing Δ for the determinant formed by the coefficients of the ϕ's and ψ's in the above equations, except those which occur in the first and last columns, we have :—

$$\Phi \begin{vmatrix} 1, & \alpha_m, & -1, & -\alpha_m, \ldots \ldots 0 \\ M, & -MN\alpha_m, & -\mu_m, & \mu_m N\alpha_m, \ldots \ldots 0 \\ 0, & 0, & 1, & \alpha_{m-1}, \ldots \ldots 0 \\ 0, & 0, & \mu_m, & -\mu_m N\alpha_{m-1}, \ldots \ldots 0 \\ & & \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \\ 0, & 0, & 0, & 0, \ldots \ldots -\alpha_1 \\ 0, & 0, & 0, & 0, \ldots \ldots \mu_1 N\alpha_1 \\ 0, & 0, & 0, & 0, \ldots \ldots \alpha_0 \\ 0, & 0, & 0, & 0, \ldots -\mu_1 N\alpha_0 \end{vmatrix} = \phi_0\Delta.$$

This may be written

$$\frac{\Phi\alpha_m}{M} \begin{vmatrix} M, & M, & -M, \ldots \ldots 0 \\ M, & -MN, & -\mu_m, \ldots \ldots 0 \\ 0, & 0, & 1, \ldots \ldots 0 \\ & & \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \\ 0, & 0, & 0, \ldots -\mu_1 N\alpha_0 \end{vmatrix} = \phi_0\Delta ;$$

whence, by subtracting the first from the second row,

$$\frac{\Phi\alpha_m}{M} \begin{vmatrix} M, & M, & -M \ldots \ldots 0 \\ 0, & -M(N+1), & M-\mu_m, \ldots \ldots 0 \\ 0, & 0, & 1, \ldots \ldots 0 \\ & & \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \\ 0, & 0, & 0, \ldots -\mu_1 N\alpha_0 \end{vmatrix} = \phi_0\Delta.$$

$$\therefore -\Phi\alpha_m(N+1)M \begin{vmatrix} 1, & \alpha_{m-1}, \ldots \ldots 0 \\ \mu_m, & -\mu_m N\alpha_{m-1}, \ldots \ldots 0 \\ & \cdot \cdot \cdot \cdot \cdot \cdot \cdot \\ 0, & 0, \quad 0, \ldots -\mu_1 N\alpha_0 \end{vmatrix} = \phi_0\Delta.$$

Proceeding in the same way with the new determinant, we finally get:—

$$\{-(N+1)\}^{m+1}\Phi\alpha_m\alpha_{m-1}\ldots\alpha_0 M\mu_m\mu_{m-1}\ldots\mu_1 = \phi_0\Delta.$$

Next, putting $\Phi = 0$, we get in like manner

$$\Psi\Delta = \{-(N+1)\}^{m+1}\psi_0\alpha_m\alpha_{m-1}\ldots\alpha_0\mu_m\mu_{m-1}\ldots\mu_1\mu_0\psi_0 ;$$

$$\therefore \quad \frac{\phi_0}{\Phi M} = \frac{\Psi}{\mu_0\psi}.$$

Hence if $M = \mu_0$, *i.e.* if the permeabilities of the enclosed and

the external space are the same, the ratios of the shielded to the unshielded fields are the same *for each harmonic term* whether the shielded field be external or internal.

The most interesting application of this proposition is to the first harmonic term.

In this case the ϕ_0 and Φ are coefficients of terms of the form rP_1, that is the field is uniform; and ψ_0 and Ψ are coefficients of terms of the form P_1/r^2, that is, the field is produced by a small magnet placed at the centre of the shells.

Hence the shielding effect on external space when a small magnet is placed at the centre of the shells is the same as the shielding effect on the enclosed space when the shells are placed in a uniform field.

In what follows I shall for the most part suppose that the magnetic forces are produced within the shells; but the above result enables the conclusions arrived at to be applied to the case of shielding against external forces.

(1) *Case of a Single Shell when the Permeabilities of the Internal and External Space are Unity.*

This case is well known, but may be included for the sake of completeness.

Since $\mu_0 = M = 1$, the equations (1) reduce to

$$\phi_1 + \psi_1\alpha_1 - \Psi\alpha_1 = 0,$$
$$\mu_1\phi_1 - N\mu_1\alpha_1\psi_1 + N\alpha_1\Psi = 0,$$
$$\phi_0 + \psi_0\alpha_0 - \phi_1 - \psi_1\alpha_0 = 0,$$
$$\phi_0 - N\alpha_0\psi_0 - \mu_1\phi_1 + N\mu_1\alpha_0\psi_1 = 0.$$

Hence Ψ/ψ_0 is the ratio of the shielded to the unshielded potential or, since this ratio is everywhere constant, that of the shielded to the unshielded field, in so far as it depends on the term under consideration, is

$$\frac{\alpha_0\mu_1(N+1)^2}{(N\mu_1+1)(N+\mu_1)\alpha_0 - N\alpha_1(\mu_1-1)^2}. \quad \cdot \quad \cdot \quad \cdot \quad (2)$$

If the unshielded field is due to a small magnet placed at the centre of the sphere, the only term in the expression for the potential is
$$A_1P_1/r^2.$$
Hence

$$n = 1, \quad N = (n+1)/n = 2, \quad \alpha_0 = a_0^{-(2n+1)} = a_0^{-3}, \quad \&c.$$

Then the above ratio becomes

$$\frac{9a_1{}^3\mu_1}{(2\mu_1+1)(2+\mu_1)a_1{}^3-2(\mu_1-1)^2a_0{}^3} = \frac{9a_1{}^3\mu_1}{9a_1{}^3\mu_1+2(\mu_1-1)^2(a_1{}^3-a_0{}^3)}.$$

If μ_1 is so great that a small integer may be neglected with regard to it, this reduces to

$$\frac{9}{2\mu_1}\frac{a_1{}^3}{a_1{}^3-a_0{}^3};$$

but this approximate form is only valid if a_1 and a_0 are not nearly equal.

It will be observed that the shielding depends only on the ratio of $a_1 : a_0$, and not on the absolute dimensions.

If the shell is thin, let $a_0 = a_1 - t$. Then, if squares and higher powers of t are neglected,

$$\frac{\Psi}{\psi_0} = \frac{3\mu_1}{3\mu_1+2(\mu_1-1)^2\dfrac{t}{a_1}}.$$

If μ_1 is not large this may be written

$$\frac{\Psi}{\psi_0} = 1 - \frac{2(\mu_1-1)^2}{3\mu_1} \cdot \frac{t}{a_1}.$$

If μ_1 is large it becomes

$$\frac{\Psi}{\psi_0} = \frac{1}{1+\dfrac{2}{3}\mu_1\dfrac{t}{a_1}}.$$

In this approximation we have neglected terms of the order $\mu_1 t^2/a_1{}^2$. The expression

$$\frac{\Psi}{\psi_0} = 1 - \frac{2}{3}\mu_1\frac{t}{a_1}$$

is only valid if terms of the order $\mu_1{}^2 t^2/a_1{}^2$ are negligible ; and as μ_1 is by supposition large, they may be very much greater than those which have already been rejected.

As an example, if $t/a_1 = 0\cdot01$, the ratio of the shielded to the unshielded field is 3/13 if $\mu_1 = 500$, and 3/23 if $\mu_1 = 1000$.

The following Table of Values is calculated for cases in which $a_1 - a_0$ is not small, on the assumption that $\mu_1 = 1000$. The corresponding numbers can be obtained in any other case when μ_1 is large by remembering that the ratio under investigation varies inversely as μ_1.

a_0/a_1.	Ψ/ψ_0.
0·9	1/60
0·8	1/108
0·7	1/146
0·6	1/174
0·5	1/194

This table illustrates the difficulty of improving the shielding by increasing the thickness of a shield already moderately thick. When the latter is increased in the ratio 5 : 1, and the internal empty space is reduced sixfold, the shielded field is only reduced in the ratio of about 1 : 3.

In general, if the volume of the material employed in a shell is seven times that of the internal spherical space the external field will be reduced to 1/100, 1/200, or 1/300 of its unshielded value, according as the permeability of the material is 500, 1000, or 1500.

Next consider the case of a small magnet placed at a distance b from the centre of the shell.

If the axis of the magnet lies on a diameter, and if the moment is ψ_0, the unshielded potential is

$$\psi_0 \left\{ \frac{P_1}{r^2} + \frac{2P_2 b}{r^3} + \frac{3P_3 b^2}{r^4} + \&c. + \frac{nP_n b^{n-1}}{r^{n+1}} + \&c. \right\},$$

where r is measured from the centre of the sphere.

To find the potential in the shielded field, we must multiply each term in the expression by the corresponding value of

$$\frac{\alpha_0 \mu_1 (N+1)^2}{(N\mu_1+1)(N+\mu_1)\alpha_0 - N\alpha_1(\mu_1-1)^2},$$

which may be called the *shielding factor*.

If the shell is thin, so that $a_0 = a_1 - t$, where t is small, this factor (remembering that $\alpha_0 = a_0^{-(2n+1)}$) becomes

$$\frac{a_1^{2n+1} \mu_1 (N+1)^2}{a_1^{2n+1} \mu_1 (N+1)^2 + (2n+1)N(\mu_1-1)^2 a_1^{2n} t}$$
$$= \frac{(2n+1)\mu_1}{(2n+1)\mu_1 + n(n+1)(\mu_1-1)^2 t/a_1},$$

which, if μ_1 is large, simplifies to

$$\frac{2n+1}{2n+1+n(n+1)\mu_1 t/a_1}.$$

Calling these shielding factors S_1, S_2, &c., the unshielded and shielded forces in the direction of the radius are given by

$$-\psi_0 \left\{ \frac{2P_1}{r^3} + \frac{2 \cdot 3P_2 b}{r^4} + \frac{3 \cdot 4 \cdot P_3 b^2}{r_3} + \&c. \right\}$$

and by

$$-\psi_0 \left\{ \frac{2P_1 S_1}{r^3} + \frac{2 \cdot 3 \cdot P_2 b S_2}{r^4} + \frac{3 \cdot 4 \cdot P_3 b^2 S_3}{r^5} + \&c. \right\}$$

respectively.

If we consider any point on the diameter on which the axis of the magnet lies and on the side towards which it is moved, all the P's are equal to unity.

The larger b becomes, the more important are the terms in which the shielding factors S_2, S_3 are small, and the more efficient is the shielding. The total force is, however, increased, as all these terms are added to the first. In other words, the force is increased owing to the approach of the magnet to the point considered, and it is only the addition to its original value which is better shielded. The average shielding is improved, but the force is increased.

The converse statement holds good for the side from which the magnet is moved. In that case the P's are alternately -1 and $+1$, the shielding is less efficient, but the force is diminished.

It may be worth while to illustrate this by a numerical example. Let the magnet be placed on a diameter at a distance from the centre = half the external radius; and let the forces be calculated at points on the same diameter, the distances of which from the exterior of the shell are also half the external radius.

Then

$$b = a_1/2, \quad r = 3a_1/2.$$

Let the thickness of the shield be 0·01 of the radius, so that $t/a_1 = 0·01$, and let the permeability be 500.

The unshielded force is :—

$$-\frac{\psi_0}{a_1^3} \{0·593\,P_1 + 0·593\,P_2 + 0·395\,P_3 + 0·219\,P_4 + 0·100\,P_5$$
$$+ 0·051\,P_6 + 0·023\,P_7 + 0·010\,P_8 + \&c.\}.$$

Multiplying each term by the corresponding shielding factor, the shielded force is :—

$$-\frac{\psi_0}{a_1^3} \{0·137\,P_1 + 0·085\,P_2 + 0·041\,P_3 + 0·018\,P_4 + 0·008\,P_5$$
$$+ 0·003\,P_6 + 0·0011\,P_7 + 0·0004\,P_8\}.$$

The true values of the unshielded forces are

$$-2\psi_0/a_1^3 \quad \text{and} \quad 2\psi_0/(2a_1)^3 = 0 \cdot 25 \psi_0/a_1^3.$$

The above series gives

$$-1 \cdot 994 \psi_0/a_1^3 \quad \text{and} \quad 0 \cdot 248 \psi_0/a_1^3,$$

which proves that the number of terms taken gives results sufficiently approximate for the purpose of illustration.

The corresponding values of the shielded forces are

$$-0 \cdot 294 \psi_0/a_1^3 \quad \text{and} \quad 0 \cdot 081 \psi_0/a_1^3.$$

These conclusions may be summed up as follows :—

Let A and B be the two external points, and let A be that towards which the magnet is moved. Then we get the results given in the following table :

Position of Magnet.	Numbers proportional to force when		Ratio.
	Unshielded.	Shielded.	
Centre	0·593 at A & B	0·137	0·23
Halfway between centre and outer boundary of shell.	2 at A	0·294	0·15
	0·25 at B	0·081	0·33

Case of Two or Three Concentric Shells of the same Permeability separated by Air-Gaps.

In the case of three shells there are twelve simultaneous equations, and we finally get :—

$$\Psi \left[\xi\eta(\eta\alpha_1 - \xi\alpha_0)\alpha_1\alpha_4(\alpha_4 - \alpha_5)(\alpha_2 - \alpha_3) \right.$$
$$+ \xi\eta(\eta\alpha_2 - \xi\alpha_3)\alpha_2\alpha_4(\alpha_0 - \alpha_1)(\alpha_4 - \alpha_5)$$
$$+ \xi\eta(\eta\alpha_5 - \xi\alpha_4)\alpha_2\alpha_3(\alpha_0 - \alpha_1)(\alpha_2 - \alpha_3)$$
$$\left. + \alpha_1\alpha_3(\xi\alpha_3 - \eta\alpha_3)(\xi\alpha_4 - \eta\alpha_5)(\xi\alpha_0 - \eta\alpha_1) \right]$$
$$= \psi_0\alpha_0\alpha_1\alpha_2\alpha_3\alpha_4(N+1)^6\mu^3, \qquad (3)$$

where $\xi = (N\mu + 1)(N + \mu)$ and $\eta = N(\mu - 1)^2$.

This reduces to the case of two shells if we put any two

consecutive α's equal to each other ; and it will be found that in all these cases the expression assumes the same form.

If $\alpha_4 = \alpha_5$, remembering that $\xi - \eta = \mu(N+1)^2$,

$$\left.\begin{aligned}
\Psi\{ -\xi\eta\alpha_2(\alpha_0 - \alpha_1)(\alpha_2 - \alpha_3) + \alpha_1(\xi\alpha_2 - \eta\alpha_3)(\xi\alpha_0 - \eta\alpha_1) \\
= \psi_0\alpha_0\alpha_1\alpha_2\mu^2(N+1)^4 \\
= \Psi D \text{ say.}
\end{aligned}\right\} \quad . \quad (4)$$

Then

$$\left.\begin{aligned}
\frac{D^2 d\Psi}{\psi_0\mu^2(N+1)^4} &= \{\xi\eta\alpha_2(\alpha_2 - \alpha_3) - \eta\alpha_1(\xi\alpha_2 - \eta\alpha_3)\}\alpha_1^2\alpha_2 d\alpha_0 \\
&+ \{-\xi\eta\alpha_2\alpha_0(\alpha_2 - \alpha_3) + \eta\alpha_1^2(\xi\alpha_2 - \eta\alpha_3)\}\alpha_0\alpha_2 d\alpha_1 \\
&+ \{\xi\eta\alpha_2^2(\alpha_0 - \alpha_1) - \eta\alpha_1\alpha_3(\xi\alpha_0 - \eta\alpha_1)\}\alpha_0\alpha_1 d\alpha_2 \\
&+ \{-\xi\eta\alpha_2(\alpha_0 - \alpha_1) + \eta\alpha_1(\xi\alpha_0 - \eta\alpha_1)\}\alpha_0\alpha_1\alpha_2 d\alpha_3.
\end{aligned}\right\} (5)$$

As α_0 and α_3 do not occur in the coefficients of $d\alpha_0$ and $d\alpha_3$ respectively, it is evident that no particular values of either these quantities give a maximum or minimum value of Ψ when the other three α's are arbitrarily selected.

Again, the coefficient of $d\alpha_0$ may be written

$$\eta\alpha_1^2\alpha_2\{\alpha_2(\xi\alpha_2 - \xi\alpha_3) - \eta\alpha_1(\xi\alpha_2 - \eta\alpha_3)\}.$$

Now $\alpha_2 < \alpha_1$, and since ξ is $> \eta$,

$$\xi\alpha_2 - \xi\alpha_3 \text{ is } < \xi\alpha_2 - \eta\alpha_3.$$

Hence this expression is always negative, *i. e.* Ψ diminishes as α_0 increases, that is as the radius a_0 diminishes.

Thus adding the permeable material within the shell so as to reduce the internal cavity always improves the shielding.

In like manner, by discussing the coefficient of $d\alpha_3$, it may be shown that an improvement is always effected by increasing the external diameter.

If, however, the smallest and largest radii are given, Ψ may be a maximum or minimum if the coefficients of $d\alpha_1$ and $d\alpha_2$ vanish ; *i. e.* if

$$\alpha_1^2 = \frac{\xi\alpha_2\alpha_0(\alpha_2 - \alpha_3)}{\xi\alpha_2 - \eta\alpha_3},$$

and

$$\alpha_2^2 = \frac{\alpha_1\alpha_3(\xi\alpha_0 - \eta\alpha_1)}{\xi(\alpha_0 - \alpha_1)}.$$

Let us first suppose that α_1 is also given, *i. e.* that the dimensions of the inner shell are fixed, then the equations enable us to determine the effect of adding another external shell of which the outer radius is also given.

We may first suppose the external shell to be of vanishing

thickness, in which case $\alpha_2 = \alpha_3$, and then allow α_2 to increase, *i. e.* the inner radius of the outer shell (a_2) to diminish.

If $\alpha_2 = \alpha_3$ the coefficient of $d\alpha_2$ is negative, for $\alpha_3 < \alpha_1$ and $\xi(\alpha_0 - \alpha_1) < \xi\alpha_0 - \eta\alpha_1$.

Hence the addition of a thin external shell reduces Ψ, *i. e.* improves the shielding.

This improvement will reach a maximum when

$$\alpha_2{}^2 = \frac{\alpha_1\alpha_3(\xi\alpha_0 - \eta\alpha_1)}{\xi(\alpha_0 - \alpha_1)};$$

but in order that this may correspond to a physical reality we must have

$$\alpha_1 > \alpha_2 > \alpha_3.$$

The first of these inequalities when combined with the above equation is equivalent to

$$\alpha_1\xi(\alpha_0 - \alpha_1) > \alpha_3(\xi\alpha_0 - \eta\alpha_1).$$

As α_1 is $> \alpha_3$ and $\xi(\alpha_0 - \alpha_1) < \xi\alpha_0 - \eta\alpha_1$, this condition may be, but is not necessarily, fulfilled.

The second is equivalent to

$$\alpha_1(\xi\alpha_0 - \eta\alpha_1) > \alpha_3\xi(\alpha_0 - \alpha_1),$$

which is always true.

Hence we conclude that if the external radius of the outer shell is so chosen that

$$\alpha_3 < \alpha_1 \frac{\xi(\alpha_0 - \alpha_1)}{\xi\alpha_0 - \eta\alpha_1},$$

there will be a maximum value of the shielding, while an air-space intervenes between the two shields. There will not be a maximum if α_3 is greater than this limit. In the case of the first harmonic the condition for a maximum becomes

$$a_3 > a_1 \left\{ \frac{\xi a_1{}^3 - \eta a_0{}^3}{\xi(a_1{}^3 - a_0{}^3)} \right\}^{\frac{1}{3}};$$

where a_0, a_1, and a_3 are the radii of the corresponding surfaces. If there is such a maximum it is evident that for some thickness of the external shell less than that which gives the best result the shielding must be the same as if the whole of the air-gap were filled.

To find this value of α_2 we have to put $\alpha_2 = \alpha_1$ in the expression for Ψ, and equate the result to the value of Ψ when α_2 is not $= \alpha_1$.

Remembering that $\mu(N+1)^2 = \xi - \eta$ we get

$$\frac{\alpha_0}{(\xi\alpha_0 - \eta\alpha_3)(\xi - \eta)} = \frac{\alpha_0\alpha_1\alpha_2}{-\xi\eta\alpha_2(\alpha_0 - \alpha_1)(\alpha_1 - \alpha_3) + \alpha_1(\xi\alpha_2 - \eta\alpha_3)(\xi\alpha_0 - \eta\alpha_1)}.$$

This leads to a quadratic in α_2, of which one root must evidently be $\alpha_2 = \alpha_1$.

The other root is

$$\alpha_2 = \alpha_3 \frac{\xi\alpha_0 - \eta\alpha_1}{\xi(\alpha_0 - \alpha_1)}.$$

If then we write $I = (\xi\alpha_0 - \eta\alpha_1)/\xi(\alpha_0 - \alpha_1)$, where I is a function only of the dimensions of the inner shell, of the permeability of the material and of the order of the harmonic term considered, we have reached the following conclusions.

If $\alpha_3 I > \alpha_1$, the shielding improves continuously as the thickness of the external shell increases from without inwards.

If $\alpha_3 I < \alpha_1$, the shielding at first improves and then deteriorates as the thickness increases.

When $\alpha_2 = \alpha_3 I$, the shielding is the same as when the whole of the space between the shells is filled, *i. e.* as when $\alpha_2 = \alpha_1$.

When $\alpha_2^2 = \alpha_1\alpha_3 I$, the shielding is a maximum, after which it diminishes until $\alpha_2 = \alpha_1$.

In the particular case when the maximum shielding is equal to that when the hollow space is just filled, the conditions $\alpha_2 = \alpha_3 I$ and $\alpha_2^2 = \alpha_1\alpha_3 I$ must be simultaneously fulfilled. Hence $\alpha_2 = \alpha_1$, and there is only one maximum, which occurs when the hollow space is just filled.

This can only be the case when

$$\alpha_2^2 = \alpha_1^2 = \frac{\alpha_1\alpha_3(\xi\alpha_0 - \eta\alpha_1)}{\xi(\alpha_0 - \alpha_1)},$$

i. e., when

$$\xi\alpha_1^2 - \alpha_1(\xi\alpha_0 + \eta\alpha_3) + \xi\alpha_0\alpha_3 = 0.$$

It may be worth while to give a numerical example to illustrate these results.

Let the small magnet be placed in the centre. Then the only harmonic term is that for which $n = 1$ and $N = 2$.

Let $\alpha_0 = 8\alpha_3 = 2\alpha,$

i. e. $a_3 = 2a_0$ and $a_1 = 1\cdot260a_0.$

Let $\mu = 501.$

Then

$$\xi = (N\mu + 1)(N + \mu) = 1003 \times 503,$$

$$\eta = N(\mu - 1)^2 = 2 \times 500^2 = \xi \text{ nearly };$$

or to a closer approximation,

$$\eta = \xi(1 - 0\cdot009).$$

Hence

$$\mathrm{I} = \frac{\xi\alpha_0 - \eta\alpha_1}{\xi(\alpha_0 - \alpha_1)} = 1 + 0\cdot009.$$

By substituting in (4) we get the values of Ψ/ψ_0 given in the following table for different values of α_2. The volumes are expressed in terms of the space enclosed by the innermost surface.

$a_2 =$	$a_2 =$	Volume of outer shell.	Total Volume.	$\Psi/\psi_0.$
$a_3 = a_0/8.$	$a_3 = 2a_0.$	0	1·00	0·018
$1\cdot009a_3 = 0\cdot1261a_0.$	$0\cdot997a_3 = 1\cdot994a_0.$	0·07	1·07	0·0102
$3a_3/2 = 3a_0/16.$	$0\cdot873a_3 = 1\cdot746a_0.$	2·66	3·66	0·0007
$2a_3 = a_0/4.$	$0\cdot794a_3 = 1\cdot588a_0.$	4·00	5·00	0·0006
$3a_3 = 3a_0/8.$	$0\cdot693a_3 = 1\cdot386a_0.$	5·33	6·33	0·0009
$a_1 = 4a_3 = a_0/2.$	$0\cdot630a_3 = 1\cdot260a_0.$	6·00	7·00	0·0102

Turning next to the case when α_1 and α_2 both vary, we may determine the maximum shielding for given external and internal radii.

The conditions to be fulfilled are :

$$\left.\begin{array}{l} -\xi\alpha_2\alpha_0(\alpha_2 - \alpha_3) + \alpha_1{}^2(\xi\alpha_2 - \eta\alpha_3) = 0 \\ \xi\alpha_2{}^2(\alpha_0 - \alpha_1) - \alpha_1\alpha_3(\xi\alpha_0 - \eta\alpha_1) = 0 \end{array}\right\} \quad . \quad . \quad (6)$$

Adding these we get either

$$\alpha_2 = \alpha_1 \quad \text{or} \quad \alpha_2\alpha_1 = \alpha_0\alpha_3.$$

The first has reference only to the point at which the maximum value is equal to that produced when all the space between the shells is filled.

The latter leads to the equation

$$\xi\alpha_2{}^3(\alpha_2 - \alpha_3) - \alpha_3{}^2\alpha_0(\xi\alpha_2 - \eta\alpha_3) = 0.$$

This equation is a biquadratic in α_2.

Since the expression is positive when $\alpha_2 = -\infty$ and negative when $\alpha_2 = \alpha_3$, there is at least one real root $< \alpha_3$, with which, since $\alpha_2 > \alpha_3$, we are not concerned.

As regards roots $> \alpha_3$, it is evident, since the whole expression is positive when $\alpha_2 = \infty$, that there is at least one real positive root $> \alpha_3$. Also, as $\xi \alpha_2 - \eta \alpha_3$ is positive, that there can only be one positive root $> \alpha_3$.

This root must be $< \alpha_1$, *i. e.* since $\alpha_2 \alpha_1 = \alpha_0 \alpha_3$, $\alpha_2^2 < \alpha_0 \alpha_3$; *i. e.* the expression must be positive when $\alpha_2^2 = \alpha_0 \alpha_3$.

This is equivalent to the condition

$$\xi \sqrt{\alpha_0}(\sqrt{\alpha_0} - \sqrt{\alpha_3}) > \sqrt{\alpha_3}(\xi \sqrt{\alpha_0} - \eta \sqrt{\alpha_3}).$$

As $\alpha_0 > \alpha_3$ and $\xi \sqrt{\alpha_0} - \xi \sqrt{\alpha_3} < \xi \sqrt{\alpha_0} - \eta \sqrt{\alpha_3}$,

this equality may be, but is not necessarily, satisfied.

Before discussing these equations further, it is convenient to modify their form.

Let

$$\frac{\alpha_0}{\alpha_1} = \frac{\alpha_2}{\alpha_3} = \lambda ; \qquad \eta = \xi(1-\epsilon) ; \qquad \frac{\alpha_0}{\alpha_3} = \mathrm{L}.$$

Then from (6),

$$\lambda^3(\lambda-1) - \mathrm{L}(\lambda-1+\epsilon) = 0, \quad . \quad . \quad . \quad (7)$$

and from (4),

$$\Psi/\psi_0 = \frac{\mu^2(\mathrm{N}+1)^4 \lambda^2 \mathrm{L}}{\xi^2\{(\lambda-1+\epsilon)^2 \mathrm{L} - (1-\epsilon)\lambda^2(\lambda-1)^2\}} ; \quad (7a)$$

or from (7),

$$\Psi/\psi_0 = \frac{\mu^2(\mathrm{N}+1)^4 \mathrm{L}^2}{\xi^2(\lambda-1)^2\{\lambda^4 - \mathrm{L}(1-\epsilon)\}} = \frac{\mathrm{L}^2 \epsilon^2}{(\lambda-1)^2\{\lambda^4 - \mathrm{L}(1-\epsilon)\}}, \quad (8)$$

since $\mu(\mathrm{N}+1)^2 = \xi - \eta = \epsilon\xi.$

In equation (8) Ψ becomes infinite when $\lambda = 1$ and when $\lambda^4 = \mathrm{L}(1-\epsilon)$.

The first of these assumptions is inconsistent with equation (7), and by substituting from $\lambda^4 = \mathrm{L}(1-\epsilon)$ in (7) we get

$$(\lambda - 1 + \epsilon)^2 = - \epsilon(1-\epsilon),$$

which is only possible if either ϵ or $1-\epsilon$ is negative, which they can never be, as ξ is always $> \eta$, and η and ξ are always positive.

In the case when the permeability is very great, $\xi = \eta = \mathrm{N}\mu^2$ nearly and ϵ may be neglected in equation (7), so that $\lambda^3 = \mathrm{L}$.

If, however, $\lambda - 1$ is very small, *i.e.* if the shells are very thin, the term in ϵ may be comparable with the others, and the approximation is not legitimate. In cases where it may

be applied we get from equation (8) the very simple result

$$\Psi/\psi_0 = \frac{(N+1)^4}{N^2\mu^2}\frac{\lambda^3}{(\lambda-1)^3} = \frac{L\epsilon^2}{(\sqrt[3]{L}-1)^3}.$$

In this case also the four quantities α_0, α_1, α_2, α_3 are in Geometrical Progression.

If $\alpha_1 = \alpha_2$, $\alpha_0/\alpha_3 = \lambda^2 = L$, so that (7) reduces to

$$(\sqrt{L}-1)^2 = \epsilon, \quad . \quad . \quad . \quad . \quad . \quad (9)$$

of which the root greater than unity is $\sqrt{L} = 1 + \sqrt{\epsilon}$.

This furnishes a limit below which the equations do not apply.

Below the limiting case lamination must be disadvantageous.

If we remove a thin slice either from the exterior or from the interior surface of a single shell, the shielding power is impaired; and if the shielding does not attain a maximum when this spherical crack is supposed to traverse the shell from inside to outside, it must always be less than if there is no crack.

Next, comparing the shielding effect of a single shell with that of a double shell of which the innermost and outermost radii are the same as that of the single shell, if we write in equation (2) α_3 for α_1, and put $\eta = \xi(1-\epsilon)$, we find by comparing with (4) that the single shell will shield best if

$$\frac{\alpha_0\epsilon}{\alpha_0-\alpha_3(1-\epsilon)} < \frac{\alpha_0\alpha_1\alpha_2\epsilon^2}{-(1-\epsilon)\alpha_2(\alpha_0-\alpha_1)(\alpha_2-\alpha_3)+\alpha_1\{\alpha_2-\alpha_3(1-\epsilon)\}\{\alpha_0-\alpha_1(1-\epsilon)\}};$$

which reduces to

$$\left(\frac{\alpha_2}{\alpha_3}-1\right)\left(\frac{\alpha_0}{\alpha_1}-1\right) < \epsilon.$$

Now if we diminish α_1, *i. e.* increase the outer radius of the inner shell, α_0/α_1 is increased; and in like manner by diminishing the inner radius of the outer shell α_2/α_3 is increased. Hence the largest value of the left-hand side of the inequality is attained when $\alpha_1 = \alpha_2$, so that if $\alpha_2/\alpha_3 = \lambda_1$, and $\alpha_0/\alpha_1 = \lambda$, $\lambda\lambda_1 = L$.

Thus

$$(\lambda_1 - 1)(\lambda - 1) = \left(\frac{L}{\lambda}-1\right)(\lambda-1),$$

of which the largest value is $(\sqrt{L}-1)^2$.

If ϵ is greater than $(\sqrt{L}-1)^2$, lamination is injurious, the limit thus fixed being the same as that previously found.

Above this limit, if for a given α_0 and α_3 we choose α_1 and α_2 so that

$$\left(\frac{\alpha_2}{\alpha_3}-1\right)\left(\frac{\alpha_0}{\alpha_1}-1\right)<\epsilon,$$

the two shells will shield better than one, *i. e.* better than if the whole of the space between the innermost and outermost surfaces were filled with the permeable material.

It of course follows *à fortiori* that the best arrangement of the two shells will, under these circumstances, give better results than the single shell, a conclusion which can be verified directly.

For we must by (8) and (2) have

$$\frac{L^2\epsilon^2}{(\lambda-1)^2\{\lambda^4-L(1-\epsilon)\}}<\frac{L\epsilon}{L-(1-\epsilon)},$$

where

$$\lambda^3(\lambda-1)-L(\lambda-1+\epsilon)=0.$$

Eliminating L, the inequality becomes

$$(1-\epsilon)\{\epsilon-(\lambda-1)^2\}^2>0.$$

which, since ϵ is always positive and <1, must always be true.

At the limiting point the curves which give the relations between L and the Ψ's for one and two shells respectively touch each other.

For, as in the case of a single shell,

$$\frac{\Psi_0}{\psi}=\frac{\epsilon L}{L-(1-\epsilon)},$$

$$\frac{1}{\psi_0}\frac{d\Psi}{dL}=-\frac{\epsilon(1-\epsilon)}{\{L-(1-\epsilon)\}^2}.$$

At the limiting point $L=(1+\sqrt{\epsilon})^2$;

$$\therefore\frac{1}{\psi_0}\frac{d\Psi}{dL}=-\frac{1-\sqrt{\epsilon}}{4(1+\sqrt{\epsilon})}.$$

In the case of two shells we have from (7),

$$\{\lambda^2(4\lambda-3)-L\}\frac{d\lambda}{dL}=\lambda-1+\epsilon,$$

and since at the limiting point $\lambda^2=L=(1+\sqrt{\epsilon})^2$,

$$\frac{d\lambda}{dL}=\frac{1}{4(1+\sqrt{\epsilon})}.$$

Also from (8),

$$\frac{1}{\psi_0}\frac{d\Psi}{dL} = \frac{2L\epsilon^2}{(\lambda-1)^2\,\lambda^4-L(1-\epsilon)} + \frac{L^2\epsilon^2(1-\epsilon)}{(\lambda-1)^2\{\lambda^4-L(1-\epsilon)\}^2}$$

$$-2\left\{\frac{1}{\lambda-1} + \frac{2\lambda^3}{\lambda^4-L(1-\epsilon)}\right\}\frac{L^2\epsilon^2}{(\lambda-1)^2\{\lambda^4-L(1-\epsilon)\}}\frac{d\lambda}{dL};$$

and if we substitute in this the values of λ, L, and $d\lambda/dL$ proper to the limiting point, we get

$$\frac{1}{\psi_0}\frac{d\Psi}{dL} = -\frac{1-\sqrt{\epsilon}}{4(1+\sqrt{\epsilon})},$$

which is the same as the value obtained in the case of the single shell.

The shielding factor in the limiting case is obtained by putting $\lambda^2 = L = (1+\sqrt{\epsilon})^2$ in (8), or in the corresponding expression for a single shell. In either case

$$\frac{\Psi}{\psi_0} = \frac{\sqrt{\epsilon}(1+\sqrt{\epsilon})}{2}.$$

Since

$$\epsilon = \frac{\xi-\eta}{\xi} = \frac{\mu(N+1)^2}{(N\mu+1)(N+\mu)},$$

which increases with N, *i. e.* with $(n+1)/n$, and therefore diminishes as n increases, the thickness of the shell at the limit is less for the higher harmonic terms, but the shielding at the limit is better.

If μ is so large, however, that we may write

$$\epsilon = \frac{(N+1)^2}{N\mu} = \frac{(2n+1)^2}{n(n+1)\mu},$$

the limiting thicknesses and the shielding factors for the principal harmonic terms vary very slowly. If $\mu=400$ we get :—

n.	ϵ.	$L=$ $(1+\sqrt{\epsilon})^2$.	$a_1/a_0=$ $(1+\sqrt{\epsilon})^{\frac{3}{2}}$.	Ψ/ψ_0.
1.	·0112	1·223	1·069	·058
2.	·0104	1·214	1·067	·056
3.	·0102	1·212	1·066	·055

Thus the limiting thickness in the case of the first three harmonic terms varies only from 6·9 per cent. to 6·6 per cent. of the radius, and the shielding factor from ·058 to ·055.

If there are three concentric shells, by differentiating the expression for Ψ in equation (3) we get

$$
\begin{aligned}
\frac{D^2 d\Psi}{\Psi_0 \mu^3 (N+1)^6 \alpha_0 \alpha_1 \alpha_2 \alpha_3 \alpha_4} \\
= \big[\xi\eta\alpha_1\alpha_4(\alpha_4-\alpha_5)\{\eta\alpha_1(\alpha_2-\alpha_3)-\alpha_2(\eta\alpha_2-\xi\alpha_3)\} \\
+ \eta\alpha_1\alpha_3(\xi\alpha_4-\eta\alpha_5)\{\xi\alpha_2(\alpha_2-\alpha_3)-\alpha_1(\xi\alpha_2-\eta\alpha_3)\}\big]\frac{d\alpha_0}{\alpha_0} \\
+ \big[\eta\alpha_3(\xi\alpha_4-\eta\alpha_5)\{(\xi\alpha_2-\eta\alpha_3)\alpha_1{}^2-\xi\alpha_0\alpha_2(\alpha_2-\alpha_3)\} \\
+ \xi\eta\alpha_4(\alpha_4-\alpha_5)\{(\eta\alpha_2-\xi\alpha_3)\alpha_0\alpha_2-\eta\alpha_1{}^2(\alpha_2-\alpha_3)\}\big]\frac{d\alpha_1}{\alpha_1} \\
+ \big[\eta\alpha_3(\xi\alpha_4-\eta\alpha_5)\{-(\xi\alpha_0-\eta\alpha_1)\alpha_1\alpha_3+\xi\alpha_2{}^2(\alpha_0-\alpha_1)\} \\
+ \xi\alpha_4(\alpha_4-\alpha_5)\{(\xi\alpha_0-\eta\alpha_1)\alpha_1\alpha_3-\eta\alpha_2{}^2(\alpha_0-\alpha_1)\}\big]\frac{d\alpha_2}{\alpha_2} \\
+ \big[\eta\alpha_3{}^2(\xi\alpha_4+\eta\alpha_5)\{\alpha_1(\xi\alpha_0-\eta\alpha_1)-\xi\alpha_2(\alpha_0-\alpha_1)\} \\
+ \xi\eta\alpha_2\alpha_4(\alpha_4-\alpha_5)\{\eta\alpha_2(\alpha_0-\alpha_1)-\alpha_1(\xi\alpha_0-\eta\alpha_1)\}\big]\frac{d\alpha_3}{\alpha_3} \\
+ \big[\eta\alpha_1(\xi\alpha_0-\eta\alpha_1)\{\xi\alpha_4{}^2(\alpha_2-\alpha_3)-\alpha_3\alpha_5(\xi\alpha_2-\eta\alpha_3)\} \\
+ \xi\eta\alpha_2(\alpha_0-\alpha_1)\{(\xi\alpha_3-\eta\alpha_2)\alpha_4{}^2+\eta\alpha_3\alpha_5(\alpha_2-\alpha_3)\}\big]\frac{d\alpha_4}{\alpha_4} \\
+ \big[\eta\alpha_1(\xi\alpha_0-\eta\alpha_1)\{\xi\alpha_4(\alpha_2-\alpha_3)+\alpha_3(\xi\alpha_2-\eta\alpha_3)\} \\
+ \xi\eta\alpha_2(\alpha_0-\alpha_1)\{(\eta\alpha_2-\xi\alpha_3)\alpha_4-\eta(\alpha_2-\alpha_3)\alpha_3\}\big]\,d\alpha_5.
\end{aligned}
\tag{10}
$$

We note that in this, as in the previous case, there can be no maximum or minimum if α_0 or α_5 are independent variables.

Further, writing the coefficient of $d\alpha_0$ in the form

$$
\eta\alpha_1\alpha_4(\xi\alpha_4-\xi\alpha_5)\{\eta\alpha_1(\alpha_2-\alpha_3)-\alpha_2(\eta\alpha_2-\xi\alpha_3)\}
$$
$$
-\eta\alpha_1\alpha_3(\xi\alpha_4-\eta\alpha_5)\{\alpha_1(\xi\alpha_2-\eta\alpha_3)-\xi\alpha_2(\alpha_2-\alpha_3)\},
$$

if we remember that the α's diminish from α_1 to α_5 and that ξ is $> \eta$, it is easy to see that the coefficient is the difference of two positive quantities of which the second is the larger.
For

$$
\xi\alpha_4-\eta\alpha_5 > \xi\alpha_4-\xi\alpha_5
$$

and

$$
\{\alpha_1(\xi\alpha_2-\eta\alpha_3)-\xi\alpha_2(\alpha_2-\alpha_3)-\{\eta\alpha_1(\alpha_2-\alpha_3)-\alpha_2(\eta\alpha_2-\xi\alpha_3)\}
$$
$$
=(\xi-\eta)\alpha_2(\alpha_1-\alpha_2),
$$

which is positive.

Hence the whole coefficient is negative, or Ψ diminishes as α_0 increases, *i. e.* as the radius a_0 diminishes. Thus, as we should expect, we obtain the same result as before, viz., that the reduction of the radius of the innermost surface always improves the shielding. In like manner if a_5 increases the shielding improves.

Let us now suppose, as before, that the outermost and innermost radii are given. The best arrangement is then found by equating the coefficients of $d\alpha_1$, $d\alpha_2$, and $d\alpha_3$, and $d\alpha_4$ to zero.

By eliminating the terms in α_4 and α_5 from the first pair, and also from the second pair of these equations, we get

$$\alpha_2\alpha_3(\alpha_1-\alpha_2)\{\xi\alpha_0(\alpha_0-\alpha_1)\alpha_2-\alpha_1^2(\xi\alpha_0-\eta\alpha_1)\}=0 \quad . \quad (11)$$

and

$$\alpha_3(\alpha_2-\alpha_3)\{\xi\eta(\alpha_0-\alpha_1)^2\alpha_2^3+(\xi\alpha_0-\eta\alpha_1)^2\alpha_1^2\alpha_3$$
$$-\xi(\xi\alpha_0-\eta\alpha_1)\alpha_1\alpha_2(\alpha_2+\alpha_3)(\alpha_0-\alpha_1)=0 \quad . \quad (12)$$

In the cross multiplications by which these equations are obtained, we assume $\alpha_4-\alpha_5 \neq 0$.

If $\alpha_1=\alpha_2$ or $\alpha_2=\alpha_3$ two of the shells are fused into one. Putting this case aside and substituting for $(\xi\alpha_0-\eta\alpha_1)/(\alpha_0-\alpha_1)$ in the second equation from the first we get

$$\alpha_1\alpha_2(\xi\alpha_0-\eta\alpha_1)-\xi\alpha_0\alpha_3(\alpha_0-\alpha_1)=0.$$

Hence and from (11),

$$\frac{\xi\alpha_0-\eta\alpha_1}{\xi\alpha_0(\alpha_0-\alpha_1)} = \frac{\alpha_3}{\alpha_1\alpha_2} = \frac{\alpha_2}{\alpha_1^2}, \quad . \quad . \quad . \quad . \quad (13)$$

$$\therefore \quad \alpha_3\alpha_1=\alpha_2^2. \quad . \quad . \quad . \quad . \quad . \quad (14)$$

Again equating the coefficient of $d\alpha_3$ to zero, substituting for $(\xi\alpha_0-\eta\alpha_1)/(\alpha_0-\alpha_1)$, rearranging the terms, and substituting again, we get

$$\frac{\xi\alpha_4-\eta\alpha_5}{\xi\alpha_4(\alpha_4-\alpha_5)} = \frac{\alpha_0\alpha_2^2}{\alpha_1^2\alpha_3^2} = \frac{\alpha_0}{\alpha_2^2} \text{ by (14),}. \quad . \quad (15)$$

Next, equating the coefficient of $d\alpha_4$ to zero, we get

$$\frac{\xi\alpha_4^2-\eta\alpha_3\alpha_5}{\alpha_4^2-\alpha_3\alpha_5} = \frac{\alpha_2}{\alpha_3}\times\frac{\xi\alpha_0-\eta\alpha_1}{\alpha_0-\alpha_1} = \frac{\xi\alpha_0}{\alpha_1}.$$

This again reduces to

$$\frac{\alpha_4^2}{\alpha_3\alpha_5}=\frac{\xi\alpha_0-\eta\alpha_1}{\xi(\alpha_0-\alpha_1)}=\frac{\alpha_0\alpha_2}{\alpha_1^2} \text{ by (13), } . \quad . \quad (16)$$

I 2

Again, since $a_2{}^2 = a_3 a_1$,

$$\therefore \quad a_3 a_1 (\xi a_4 - \eta a_5) = \xi a_0 a_4 (a_4 - a_5). \quad . \quad . \quad . \quad (17)$$

But

$$a_3 a_5 (\xi a_0 - \eta a_1) = \xi a_4{}^2 (a_0 - a_1),$$

or

$$\xi a_0 (a_3 a_5 - a_4{}^2) = a_1 (\eta a_3 a_5 - \xi a_4{}^2).$$

Multiplying this by (17) and putting $a_2{}^2 = a_3 a_1$,

$$a_3 (\xi a_4 - \eta a_5)(a_3 a_5 - a_4{}^2) = a_4 (a_4 - a_5)(\eta a_3 a_5 - \xi a_4{}^2),$$

$$\therefore \quad (a_3 - a_4)\{ a_3 a_5 (\xi a_4 - \eta a_5) - \xi a_4{}^2 (a_4 - a_5) \} = 0.$$

If $a_3 = a_4$ the problem is reduced to the case of two shells.
If $a_3 \neq a_4$,

$$\frac{\xi a_4 - \eta a_5}{\xi (a_4 - a_5)} = \frac{a_4{}^2}{a_3 a_5}. \quad . \quad . \quad . \quad . \quad (18)$$

Hence the equations (13), (15), (16), and (18) finally reduce to

$$\frac{\xi a_0 - \eta a_1}{\xi (a_0 - a_1)} = \frac{a_3 a_0}{a_1 a_2} = \frac{a_2 a_0}{a_1{}^2} = \frac{a_4{}^2}{a_3 a_5} = \frac{a_0 a_4}{a_2{}^2}. \quad . \quad . \quad (19)$$

It must be remembered that in obtaining these equations we have thrown out the alternative cases where any two consecutive values of a become identical; *i. e.* cases in which the three shells become two, either by fusion or by the dispearance of one.

Thus the solution for the case of two shells is contained in the general equations for three shells, but the equality of the above groups of ratios holds good only when there are three.

It remains to assure ourselves that in the case of three shells all the variables give minima simultaneously.

Thus, considering the coefficient of da_1 the coefficient of $a_1{}^2$ is

$$\eta a_3 (\xi a_4 - \eta a_5)(\xi a_2 - \eta a_3)$$

$$- \eta a_4 (\xi a_4 - \xi a_5)(\eta a_2 - \eta a_3).$$

Comparing these term by term, we see that the terms are either equal or are less in the second expression. Hence the coefficient of $a_1{}^2$ is positive. If, then, a_1 is a little less than the critical value, the coefficient of da_1 must be negative. Hence, as a_1 increases up to the critical value Ψ diminishes, *i. e.* the critical value of a_1 corresponds to a minimum.

The other coefficients if treated in the same way lead to the same conclusion. We may now proceed to put equation (19) into the simplest form for calculation.

Since

$$\frac{\alpha_2}{\alpha_3} = \frac{\alpha_1}{\alpha_2},$$

$$\therefore \quad \frac{\alpha_4}{\alpha_3 \alpha_5} = \frac{\alpha_0}{\alpha_2{}^2} = \frac{\alpha_0}{\alpha_1 \alpha_3}, \quad \therefore \quad \frac{\alpha_4}{\alpha_5} = \frac{\alpha_0}{\alpha_1},$$

and since

$$\frac{\alpha_2 \alpha_0}{\alpha_1{}^2} = \frac{\alpha_4{}^2}{\alpha_3 \alpha_5}, \quad \therefore \quad \frac{\alpha_2}{\alpha_1} = \frac{\alpha_4}{\alpha_3};$$

so that we have three independent equations, viz.,

$$\left. \begin{array}{l} \dfrac{\alpha_0}{\alpha_1} = \dfrac{\alpha_4}{\alpha_5} = \lambda \text{ say,} \\[2mm] \dfrac{\alpha_1}{\alpha_2} = \dfrac{\alpha_2}{\alpha_3} = \dfrac{\alpha_3}{\alpha_4} = \lambda' \text{ say,} \end{array} \right\} \quad . \quad . \quad . \quad (20)$$

and

together with

$$(\xi\lambda - \eta)\lambda' = \xi(\lambda - 1)\lambda \; ; . \quad . \quad . \quad . \quad (21)$$

also

$$\frac{\alpha_0}{\alpha_5} = \lambda^2 \lambda'^3 = L \text{ say as before.}$$

So that equation (21) becomes

$$(\xi\lambda - \eta)\, L^{\frac13} = \xi(\lambda - 1)\lambda^{\frac23}$$

or

$$(\lambda - 1 + \epsilon)\, L^{\frac13} = (\lambda - 1)\lambda^{\frac23}. \quad . \quad . \quad . \quad (22)$$

If $\lambda' = 1$ all the shells fuse into one (without passing through the intermediate stage of two shells). In this case $\lambda^2 = L$.

Substituting in (22) we get

$$(\sqrt{L} - 1)^2 = \epsilon,$$

which is the same as (9).

Thus the ratio of the outermost to the innermost radius below is the same for two and for three shells.

The maxima of advantage in the two cases are independent, and to determine between them their magnitudes must be compared.

Substituting in (3) from equation (20) and simplifying by means of (22), we finally get

$$\frac{\Psi}{\Psi_0} = \frac{\epsilon^3 L^{\frac43}}{(\lambda - 1)^4 \{\lambda^{\frac23} - L^{\frac13}(1 - \epsilon)\}}, \quad . \quad . \quad (23)$$

where λ is given by equation (22).

In the limiting case when $\lambda^2 = L = (1 + \sqrt{\epsilon})^2$,

$$\Psi/\psi_0 = \frac{\sqrt{\epsilon}(1 + \sqrt{\epsilon})}{2},$$

which is, as it should be, the same as the value obtained by inserting the same values of λ and L in the corresponding expression for two shells. When ϵ is negligible as compared with λ and L we get from (22) $\lambda^5 = L$, and from (23)

$$\frac{\Psi}{\psi_0} = \frac{\epsilon^3 L}{(\sqrt[5]{L}-1)^5} = \frac{\epsilon^3 \lambda^5}{(\lambda-1)^5} = \frac{(N+1)^6}{N^3 \mu^3} \times \frac{L}{(\sqrt[5]{L}-1)^5}.$$

If we take the numbers before employed, viz. :—

$$\mu = 501, \quad \alpha_0 = 8\alpha_3, \quad N = 2,$$

we have $\qquad \lambda = \sqrt[5]{8} = 1\cdot516$;

$$\therefore \quad \frac{\Psi}{\psi_0} = \frac{3^6}{500^3} \times \left(\frac{1}{0\cdot516}\right)^5 = 0\cdot00016.$$

The results so far obtained in the special case to which numerical calculation has been applied may be summed up as follows, the arrangement being the best in each case :—

	Volume of Material used.	External Field.
Single shell	1·0	0·018
Two shells...............	5·0	0·0006
Three shells	4·8	0·00016
Single shell	7·0	0·0102

The great advantage of the lamination of the shielding material is here well exhibited.

As the external field varies slowly in the neighbourhood of the minimum, a considerable economy of material may be effected without much sacrifice of efficiency. Thus, in the case of two shells, we have seen that whereas to secure the minimum external field (0·0006 of the unshielded field) the volume of the material used must (in the case considered) be five times the internal volume, a practically identical result (0·0007) can be obtained by the use of a volume 3·66, while an efficiency four times greater can be obtained by a volume 4·8.

Best arrangement in the form of Two Shells separated by an Air-gap when the innermost radius and the volume of the material are given.

So far I have supposed that both the innermost and outermost radii are given.

It is evident that we may reduce the number of the independent variables, and I now proceed to discuss two problems which might occur in practice. The enunciation of the first of these is given above.

In neither case is the solution very simple, and I therefore confine myself to the case of two shells when the magnet is in the centre. In this case $\alpha_1 = 1/a_1{}^3$ &c., so that the condition that the volume shall be constant is

$$\frac{1}{\alpha_3} - \frac{1}{\alpha_2} + \frac{1}{\alpha_1} - \frac{1}{\alpha_\theta} = \frac{1}{R} \text{ say.}$$

Hence

$$\frac{d\alpha_3}{\alpha_3{}^2} - \frac{d\alpha_2}{\alpha_2{}^2} + \frac{d\alpha_1}{\alpha_1{}^2} = 0.$$

Substituting for $d\alpha_2$ in equation (5), and remembering that $d\alpha_0 = 0$, we get as the conditions for a critical value

$$\xi\alpha_2(\alpha_0 - \alpha_1)\{\alpha_2{}^2 - \alpha_3{}^2\} - \alpha_1\alpha_3(\alpha_2 - \alpha_3)(\xi\alpha_0 - \eta\alpha_1) = 0 \quad . \quad (24)$$

and

$$\{-\xi\eta\alpha_1\alpha_0(\alpha_2 - \alpha_3) + \eta\alpha_1{}^2(\xi\alpha_2 - \eta\alpha_3)\}\alpha_1$$
$$+ \{\xi\eta\alpha_2{}^2(\alpha_0 - \alpha_1) - \eta\alpha_1\alpha_3(\xi\alpha_0 - \eta\alpha_1)\}\alpha_2 = 0. \quad . \quad . \quad (25)$$

From the first of these we get

$$(\xi\alpha_0 - \eta\alpha_1)\alpha_1\alpha_3 = \xi\alpha_2(\alpha_0 - \alpha_1)(\alpha_2 + \alpha_3). \quad . \quad . \quad . \quad (26)$$

Substituting for $\xi\alpha_0 - \eta\alpha_1$ in (25),

$$(\xi\alpha_2 - \eta\alpha_3)\alpha_1{}^3 = \xi\alpha_2\{\alpha_0\alpha_1(\alpha_2 - \alpha_3) + \alpha_2\alpha_3(\alpha_0 - \alpha_1)\},$$

multiply by α_1 and subtract,

$$\therefore \quad \alpha_1{}^2(\alpha_0\alpha_3 - \alpha_1\alpha_2) = \alpha_2\{-\alpha_0\alpha_1(\alpha_2 - \alpha_3)$$
$$+ (\alpha_0 - \alpha_1)(\alpha_1\alpha_2 + \alpha_1\alpha_3 - \alpha_2\alpha_3)\} ;$$
$$\therefore \quad \alpha_1(\alpha_0\alpha_3 - \alpha_1\alpha_2) = \alpha_2\alpha_3(\alpha_0 - \alpha_1),$$

or

$$\alpha_0\alpha_3(\alpha_1 - \alpha_2) = \alpha_1\alpha_2(\alpha_1 - \alpha_3). \quad . \quad . \quad . \quad (27)$$

But

$$\frac{1}{\alpha_3} - \frac{1}{\alpha_2} + \frac{1}{\alpha_1} - \frac{1}{\alpha_0} = \frac{1}{R},$$

or
$$(\alpha_0 - \alpha_3)\alpha_2\alpha_1 - (\alpha_1 - \alpha_2)\alpha_0\alpha_3 = \frac{\alpha_0\alpha_1\alpha_2\alpha_3}{R};$$

$\therefore$ by (27), $\alpha_2\alpha_1\{\alpha_0 - \alpha_3 - (\alpha_1 - \alpha_3)\} = \frac{\alpha_0\alpha_1\alpha_2\alpha_3}{R}$;

$$\therefore \quad \alpha_0 - \alpha_1 = \frac{\alpha_0\alpha_3}{R}. \quad . \quad . \quad . \quad . \quad (28)$$

Hence
$$\alpha_1 = \alpha_0\left(1 - \frac{\alpha_3}{R}\right).$$

By combining this with (27),

$$\alpha_2\left\{\alpha_0\left(1 - \frac{\alpha_3}{R}\right)^2 + \frac{\alpha_3^2}{R}\right\} = \alpha_0\alpha_3\left(1 - \frac{\alpha_3}{R}\right); \quad . \quad (29)$$

also from (26) and (28),

$$(\xi\alpha_0 - \eta\alpha_1)\alpha_1 = \frac{\xi\alpha_2\alpha_0}{R}(\alpha_2 + \alpha_3),$$

and substituting for α_2 from (29), and dividing by $1 - \frac{\alpha_3}{R}$, this becomes

$$\left\{\xi - \eta + \frac{\eta\alpha_3}{R}\right\}\left\{\alpha_0^2\left(1 - \frac{\alpha_3}{R}\right)^3 + \frac{2\alpha_0\alpha_3^2}{R}\left(1 - \frac{\alpha_3}{R}\right)\right\}$$
$$-\frac{\xi}{R}\alpha_3^2\alpha_0\left\{2 - \frac{\alpha_3}{R}\right\} - \frac{\eta\alpha_3^4}{R^2} = 0. \quad . \quad . \quad . \quad (30)$$

The coefficient of α_3^4 in this expression is negative when $\alpha_3 = -\infty$.

It is positive when $\alpha_3 = 0$, and negative when $\alpha_3 = \infty$.

Hence the equation has a positive root. In order that the solution may be applicable, this root must be such that

$$\frac{1}{\alpha_3} - \frac{1}{\alpha_0} > \frac{1}{R};$$

i. e. the space enclosed between the inner boundary of the inner shell and the outer boundary of the outer one must be greater than the volume of the material used. The change in the sign of the expression from positive to negative as α_3 increases must therefore take place when

$$\frac{1}{\alpha_3} > \frac{1}{\alpha_0} + \frac{1}{R},$$

or the expression must be negative when

$$\frac{1}{\alpha_3} = \frac{1}{\alpha_0} + \frac{1}{R}.$$

Now equation (30) may be thrown into the form

$$\left(\frac{\xi-\eta}{\alpha_3}+\frac{\eta}{R}\right)\left\{\alpha_0^2\left(\frac{1}{\alpha_3}-\frac{1}{R}\right)^3+\frac{2\alpha_0}{R}\left(\frac{1}{\alpha_3}-\frac{1}{R}\right)\right\}$$
$$-\frac{\xi}{R}\frac{\alpha_0}{\alpha_3}\left(\frac{2}{\alpha_3}-\frac{1}{R}\right)-\frac{\eta}{R^2}=0 ;$$

and putting

$$\frac{1}{\alpha_3}-\frac{1}{R}=\frac{1}{\alpha_0},$$

the left-hand side becomes

$$\xi\left(\frac{1}{R}+\frac{1}{\alpha_0}\right)^2\left\{\frac{\xi-\eta}{\xi}-\frac{\alpha_0}{R}\right\}.$$

Hence the condition that there shall be an arrangement which gives a minimum external field is that

$$\frac{\alpha_0}{R}>\frac{\xi-\eta}{\xi}, \quad i.e. >\epsilon, \quad i.e. >\frac{9\mu}{(2\mu+1)(2+\mu)}.$$

If we confine ourselves to the case of a small magnet in the centre of the shell: in the limiting case

$$L=\frac{\alpha_0}{\alpha_3}=1+\frac{\alpha_0}{R}=1+\epsilon,$$

as against

$$L=(1+\sqrt{\epsilon})^2,$$

obtained when the internal and external radii were given.

If μ is nearly equal to unity, this reduces to

$$\frac{1}{R}>\frac{1}{\alpha_0} ;$$

i. e. there will be no " best arrangement " unless the volume of the shielding material exceeds the volume of the space enclosed. If μ is very large, the expression becomes

$$\frac{1}{R}>\frac{1}{\alpha_0}\times\frac{9}{2\mu}.$$

Thus, if $\mu=500$, $\quad\dfrac{1}{R}>\dfrac{0\cdot009}{\alpha_0}.$

There will be no " best arrangement " unless the volume of the shielding material is greater than (in round numbers) one hundreth of the volume enclosed ; *i. e.* unless it is more than sufficient to form a shell the thickness of which is $=0\cdot003$ of the radius.

In this case therefore, as in that in which the radius of the

outer surface was given, if very thin shells are used, lamination is injurious. The higher the permeability the smaller is the lower limit of thickness above which lamination is useful. If the permeability is great, the limit is $\dfrac{3}{2\mu} \times$ radius. If we put

$$\frac{1}{\alpha_3} = \frac{1}{R} + \frac{1}{\alpha_0}$$

in equation (29), we get $\alpha_2 = \alpha_3$, *i. e.* the thickness of the external shell vanishes in the limiting case.

I now proceed to give some numerical examples of the application of these formulæ. Equation (30) is troublesome, but when μ is large so that ξ and η are nearly equal it may be simplified.

It then reduces to

$$\alpha_0{}^2\left(\frac{1}{\alpha_3}-\frac{1}{R}\right)^3 + \frac{2\alpha_0}{R}\left(\frac{1}{\alpha_3}-\frac{1}{R}\right) - \frac{\alpha_0}{\alpha_3}\left(\frac{2}{\alpha_3}-\frac{1}{R}\right) - \frac{1}{R} = 0. \quad . \quad . \quad (31)$$

We have already seen that when the radius of the outer shell is twice the smallest radius, the best result is obtained when the volume of the shells is five times the volume of the space enclosed by the smaller shell.

The above equation may be used to determine whether a still better arrangement is possible with the same volume of material, if we suppose the radius of the external surface variable.

If $\alpha_0 = 1$, $1/R = 5$, and equation (31) is found to have a root such that

$$1/\alpha_3 = 9{\cdot}5 \text{ nearly.}$$

This gives

$$\alpha_3 = \sqrt[3]{9{\cdot}5} = 2{\cdot}118 \,;$$

and, as in the previous calculation we assumed $\alpha_3 = 2$, it is evident that the two critical points nearly coincide.

In this case we get

$$\alpha_1 = \alpha_0(1 - \alpha_3/R) = 9/19,$$

from $$\alpha_2 = 18/101.$$

The magnitude of the shielded field is practically the same as before.

It must be remembered that neither the equation in α_3 nor the ratio Ψ/ψ_0 are valid when ξ is put $= \eta$ if the shells are thin or (which amounts to the same thing) if R is large.

The best method of dealing with the problem is, then, as follows :—

Write $\xi = \eta(1 + \epsilon)$,

where ϵ is so small that terms in ϵ may be neglected, unless divided by a small quantity.

Then equation (30) may be written

$$\left(1 + \frac{\epsilon R}{\alpha_3}\right)\left\{\alpha_0{}^2\left(\frac{1}{\alpha_3} - \frac{1}{R}\right)^3 + \frac{2\alpha_0}{R}\left(\frac{1}{\alpha_3} - \frac{1}{R}\right)\right\}$$
$$- \frac{\alpha_0}{\alpha_3}\left(\frac{2}{\alpha_3} - \frac{1}{R}\right)(1 + \epsilon) - \frac{1}{R} = 0.$$

The terms in ϵ may therefore be neglected unless R/α_3 is large.

As an example, let $R = 10$, *i.e.* let the volume of the metal be one tenth of the volume of the enclosure.

If then, as before, we take $\mu = 501$, $\alpha_0 = 1$,

$$\therefore \quad \xi = \eta(1 + 0.009) \quad \text{and} \quad \epsilon = 0.009.$$

If we neglect all the terms in ϵ we get

$$\frac{1}{\alpha_3} = 2.17.$$

Hence $$\epsilon R/\alpha_3 = .1953,$$

which cannot be neglected when compared with unity.

Taking this term into account,

$$1/\alpha_3 = 1.875.$$

As the radii vary inversely as the cube roots of the α's, the two values of the external radius are 1.233 and 1.294. As the shielding varies slowly when near a minimum value, as the outer shell is displaced outward, it is probable that no very grave error would be introduced even in this case by the use of the approximate equation. The error would, however, increase rapidly as the volume of material employed diminished.

Using the more correct value we get

$$\alpha_1 = \alpha_0\left(1 - \frac{\alpha_3}{R}\right) = 1 - 0.0533 = 0.9467,$$
$$-\frac{1}{\alpha_2} = \frac{1}{R} - \frac{1}{\alpha_3} - \frac{1}{\alpha_1} + \frac{1}{\alpha_0} = 0.1 - 1.875 - 1.056 + 1 = -1.831.$$

Hence we have for the best arrangement,

$$\alpha_3 = 0.5333, \quad \alpha_2 = 0.5461, \quad \alpha_1 = 0.9467, \quad \alpha_0 = 1,$$
or $$\alpha_3 = 1.233, \quad \alpha_2 = 1.223, \quad \alpha_1 = 1.018, \quad \alpha_0 = 1.$$

It will be convenient to throw equation (4) into a form suitable for calculation when the shells are thin and the permeability is great.

With the same notation as that just employed it becomes

$$\Psi(\alpha_0-\alpha_1)(\alpha_2-\alpha_3)\left\{-\alpha_2+\alpha_1\left(1+\frac{\alpha_3\epsilon}{\alpha_2-\alpha_3}\right)\left(1+\frac{\alpha_1\epsilon}{\alpha_0-\alpha_1}\right)\right\}$$
$$=\frac{\psi_0\alpha_0\alpha_1\alpha_2(N+1)^4}{N^2\mu^2},$$

which, in the case under consideration, leads to the result

$$\Psi/\psi_0=0\cdot064.$$

By (2), if the same amount of material were concentrated in a single shell, we should have

$$\Psi/\psi_0=0\cdot089.$$

In this case therefore the advantage of the best arrangement is much less than if a larger amount of material were used.

No very great disadvantage is entailed in such a case if the outer shell be outside its best position, as, if we take $1/\alpha_3=3$, we get

$$\Psi/\psi_0=0\cdot069,$$

which does not differ very much from the minimum value.

Case of Two Shells when the largest and smallest radii and the volume of the material used are given.

In this case $d\alpha_0=d\alpha_3=0$, and as before

$$\frac{1}{\alpha_3}-\frac{1}{\alpha_2}+\frac{1}{\alpha_1}-\frac{1}{\alpha_0}=\frac{1}{R},$$
$$\frac{1}{\alpha_2}-\frac{1}{\alpha_1}=\frac{1}{\rho},$$

where, since α_3 and α_0 are given, ρ is a known quantity.

Hence substituting from

$$\frac{d\alpha_2}{\alpha_2^2}=\frac{d\alpha_1}{\alpha_1^2} \text{ in (5)}$$

we get

$$[\xi\eta\{\alpha_1\alpha_2(\alpha_1+\alpha_2)-\alpha_0\alpha_2^2\}-\eta^2\alpha_1^2\alpha_3](\alpha_2-\alpha_3)=0,$$

or

$$\alpha_2^2(\alpha_0-\alpha_1)-\alpha_2\alpha_1^2=-\frac{\eta}{\xi}\alpha_1^2\alpha_3.$$

But
$$\frac{1}{\alpha_2} = \frac{\rho + \alpha_1}{\rho \alpha_1},$$

$$\therefore \quad \frac{\rho^2(\alpha_0 - \alpha_1)}{(\rho + \alpha_1)^2} - \frac{\rho \alpha_1}{\rho + \alpha_1} = -\frac{\eta \alpha_3}{\xi},$$

or
$$(\rho + \alpha_1)^2 = \frac{\xi \rho^2 (\alpha_0 + \rho)}{\xi \rho - \eta \alpha_3},$$

whence α_1 is known.

In the case when μ is so great that ξ may be taken $= \eta$, this becomes

$$(\rho + \alpha_1)^2 (\rho - \alpha_3) = \rho^2 (\alpha_0 + \rho).$$

If the given volume is very nearly $= \frac{4}{3}\pi(a_3^3 - a_0^3)$, $1/\rho$ is small.

In this case the solution reduces to

$$2\alpha_1 \xi - \eta \alpha_3 = \xi \alpha_0,$$

or
$$\alpha_1 = \frac{\alpha_3 \eta + \xi \alpha_0}{2\xi}.$$

If μ is large, this becomes

$$\alpha_1 = \frac{\alpha_3 + \alpha_0}{2} \qquad \text{or} \qquad \frac{1}{a_1^3} = \frac{1}{2}\left(\frac{1}{a_3^2} + \frac{1}{a_0^2}\right).$$

Hence, if the external and internal radii are given, the best position for a narrow crack within the shell is such that the volume it encloses is the harmonic mean of the volumes enclosed by the inner and outer surfaces of the shell respectively.

Case of Two contiguous Shells of different Permeabilities.

It is evident that the question as to the best arrangement of two shells of different permeabilities cannot be very definitely answered.

If the dimensions of the shells are variable, the more of the more permeable material we use, the more complete will be the shielding.

If, however, the dimensions of the shells are fixed, under certain circumstances (such as when its thickness is much the greater) it will be better to make the outer shell of the more permeable material, while under other conditions the reverse arrangement may be best.

Though the problem is not of any great practical interest, it may be worth while to indicate the mode of solution.

Let $\mu_0 = \mu_3 = 1$, and let the permeabilities of the two shells be μ and μ_2. Then we get

$$\Psi\{-\alpha_1\alpha_2N(N\mu_1+\mu_2)(\mu_2-1)(\mu_1-1)-\alpha_1{}^2N(N+\mu_2)(\mu_1-\mu_2)(\mu_1-1)$$
$$+\alpha_0\alpha_2(N\mu_1+1)N(\mu_2-1)(\mu_1-\mu_2)+\alpha_0\alpha_1(N\mu_1+1)(N+\mu_2)(N\mu_2+\mu_1)\}$$
$$=\psi_0\alpha_0\alpha_1(N+1)^3\mu_1\mu_2.$$

Hence, if Ψ_2 and Ψ_1 be the external potential when the permeability of the external shell is μ_2 and μ_1 respectively, we get, by exchanging the positions of the symbols μ_1 and μ_2 in the above expression and subtracting,

$$\psi\alpha_0\alpha_1(N+1)^3\mu_1\mu_2\left\{\frac{1}{\Psi_2}-\frac{1}{\Psi_1}\right\}$$
$$=(\mu_1-\mu_2)\left[-\alpha_1{}^2N\{2\mu_1\mu_2+(N-1)(\mu_1+\mu_2)-2N\}\right.$$
$$-\alpha_1(\alpha_2+\alpha_0)N(N-1)(\mu_2-1)(\mu_1-1)$$
$$\left.+\alpha_0\alpha_2N\{2N\mu_1\mu_2-(N-1)(\mu_1+\mu_2)-2\}\right].$$

Hence the exchange of materials causes no difference if either $\mu_1=\mu_2$ or if the second factor on the right-hand side vanishes.

If both the shells are thin let $a_2=a_1+t_1$, and $a_0=a_1-t_0$, where the squares of t_1 and t_2 may be neglected.

Then

$$\alpha_2=(a_1+t_2)^{-(2n+1)}=\alpha_1\left\{1-(2n+1)\frac{t_2}{a_1}\right\}$$
$$\alpha_0=(a_1-t_0)^{-(2n+1)}=\alpha_1\left\{1+(2n+1)\frac{t_0}{a_1}\right\}.$$

Substituting these approximate values, the second factor becomes

$$-(2n+1)N(N+1)(\mu_1\mu_2-1)(t_2-t_0)/a_1,$$

which proves that, as we should expect, if the shells are thin the order of their arrangement is indifferent.

Case of Three Shells of different Permeabilities.

The general relation between Ψ and ψ_0 when an internal space of permeability μ_0 is surrounded by three concentric spherical shells of permeabilities μ_1, μ_2, μ_3, and when the permeability of external space is μ_4, is

$$\psi_0\alpha_0\alpha_1\alpha_2 . \mu_0\mu_1\mu_2\mu_3(N+1)^4/\Psi$$
$$=\alpha_1\alpha_2\alpha_3N(\mu_3-\mu_4)(\mu_0-\mu_1)(N\mu_2+\mu_3)(N\mu_1+\mu_2)$$
$$+\alpha_1\alpha_2{}^2N(N\mu_4+\mu_3)(\mu_2-\mu_3)(\mu_0-\mu_1)(N\mu_1+\mu_2)$$
$$+\alpha_1{}^2\alpha_3N^2(\mu_3-\mu_4)(\mu_2-\mu_3)(\mu_1-\mu_2)(\mu_0-\mu_1)$$
$$+\alpha_1{}^2\alpha_2N(N\mu_4+\mu_3)(N\mu_3+\mu_2)(\mu_1-\mu_2)(\mu_0-\mu_1)$$
$$+\alpha_0\alpha_2\alpha_3N(N\mu_2+\mu_3)(N\mu_1+\mu_0)(\mu_3-\mu_4)(\mu_1-\mu_2)$$
$$+\alpha_0\alpha_2{}^2N(N\mu_4+\mu_3)(N\mu_1+\mu_0)(\mu_2-\mu_3)(\mu_1-\mu_2)$$
$$+\alpha_0\alpha_1\alpha_3N(N\mu_2+\mu_1)(N\mu_1+\mu_0)(\mu_3-\mu_4)(\mu_2-\mu_3)$$
$$+\alpha_0\alpha_1\alpha_2(N\mu_1+\mu_0)(N\mu_2+\mu_1)(N\mu_3+\mu_2)(N\mu_4+\mu_3).$$

If now we put $\mu_0=\mu_2=\mu_4=1$, this reduces to the case of two concentric shells of permeabilities μ_1 and μ_3 respectively in air and separated by an air-gap. The equation then becomes

$$
\begin{aligned}
\psi_0\alpha_0\alpha_1\alpha_2 \, . \, &\mu_1\mu_3(N+1)^4/\Psi \\
={}&-\alpha_1\alpha_2\alpha_3 N(\mu_3-1)(\mu_1-1)(N+\mu_3)(N\mu_1+1) \\
&+\alpha_1\alpha_2{}^2 N(N+\mu_3)(\mu_3-1)(\mu_1-1)(N\mu_1+1) \\
&+\alpha_1{}^2\alpha_3 N^2(\mu_3-1)^2(\mu_1-1)^2 \\
&-\alpha_1{}^2\alpha_2 N(N+\mu_3)(N\mu_3+1)(\mu_1-1)^2 \\
&+\alpha_0\alpha_2\alpha_3 N(N+\mu_3)(N\mu_1+1)(\mu_3-1)(\mu_1-1) \\
&-\alpha_0\alpha_2{}^2 N(N+\mu_3)(N\mu_1+1)(\mu_3-1)(\mu_1-1) \\
&-\alpha_0\alpha_1\alpha_3 N(N+\mu_1)(N\mu_1+1)(\mu_3-1)^2 \\
&+\alpha_0\alpha_1\alpha_2(N\mu_1+1)(N+\mu_1)(N\mu_3+1)(N+\mu_3).
\end{aligned}
$$

If we write

$$
\begin{aligned}
\xi_1&=(N\mu_1+1)(N+\mu_1), &\xi_3&=(N\mu_3+1)(N+\mu_3), \\
\eta_1&=N(\mu_1-1)^2, &\eta_3&=N(\mu_3-1)^2, \\
P&=N(\mu_3-1)(\mu_1-1)(N+\mu_3)(N\mu_1+1),
\end{aligned}
$$

the equation reduces to

$$
\begin{aligned}
&\psi_0\alpha_0\alpha_1\alpha_2\mu_1\mu_3(N+1)^4\Psi \\
&=\alpha_1(\xi_3\alpha_2-\eta_3\alpha_3)(\xi_1\alpha_0-\eta_1\alpha_1)-P\alpha_2(\alpha_0-\alpha_1)(\alpha_2-\alpha_3),
\end{aligned}
$$

which, if we proceed to put $\mu_1=\mu_3$, further reduces to the expression previously obtained.

Differentiating,

$$
\left.
\begin{aligned}
&\frac{D^2 d\Psi}{\psi_0\mu_1\mu_3(N+1)^4} \\
&=\{P\alpha_2\alpha_1(\alpha_2-\alpha_3)-\eta\alpha_1{}^2(\xi_3\alpha_2-\eta_3\alpha_3)\}\alpha_1\alpha_2 d\alpha_0 \\
&+\{-P\alpha_2\alpha_0(\alpha_2-\alpha_3)+\eta_1\alpha_1{}^2(\xi_3\alpha_2-\eta_3\alpha_3)\}\alpha_0\alpha_2 d\alpha_1 \\
&+\{P\alpha_2{}^2(\alpha_0-\alpha_1)-\eta_3\alpha_1\alpha_3(\xi_1\alpha_0-\eta_1\alpha_1)\}\alpha_0\alpha_1 d\alpha_2 \\
&+\{-P\alpha_2(\alpha_0-\alpha_1)+\eta\alpha_1(\xi_1\alpha_0-\eta_1\alpha_1)\}\alpha_0\alpha_1\alpha_2 d\alpha_3.
\end{aligned}
\right\} \quad (32)
$$

If the inner shell and the external radius are given, the best value of $\alpha_2{}^2$ is deduced from the equation

$$
\alpha_2{}^2=\frac{\eta_3}{P}\cdot\frac{\alpha_1\alpha_3}{\alpha_0-\alpha_1}(\xi_1\alpha_0-\eta_1\alpha_1).
$$

Comparing this with equation (6) we see that the new value of α_2 is greater than that obtained when the permeability of the external shell is the same as that of the inner one if

$$
\eta_3/P>1/\xi_1;
$$

i. e., if $(\mu_3 - 1)(N + \mu_1) > (\mu_1 - 1)(N + \mu_3)$,

i. e., if $\mu_3 > \mu_1$.

In like manner, if the outer shell and the internal radius of the inner shell are given, the best arrangement requires that

$$\alpha_1{}^2 = \frac{P\alpha_2\alpha_0(\alpha_2 - \alpha_3)}{\eta_1(\xi_3\alpha_2 - \eta_3\alpha_3)},$$

which is greater than the corresponding value when the permeabilities of the shells are the same as that of the inner shell if

$$\frac{P}{\eta_1(\xi_3\alpha_2 - \eta_3\alpha_3)} > \frac{\xi_1}{\xi_1\alpha_2 - \eta_1\alpha_3},$$

i. e., if $\alpha_2\xi_1(P - \eta_1\xi_3) > \alpha_3\eta_1(P - \xi_1\eta_3)$.

But

$$P - \eta_1\xi_3 = N(\mu_1 - 1)(N + \mu_3)(N + 1)(\mu_3 - \mu_1),$$
$$P - \xi_1\eta_3 = N(\mu_3 - 1)(N\mu_1 + 1)(N + 1)(\mu_1 - \mu_3);$$

and therefore the two sides of the inequality are always of opposite signs.

Hence, if the permeability of the outer shell is increased, the values of α_2 and α_1 corresponding to the best arrangement under the circumstances supposed increase, i. e., the outer shell increases and the inner shell diminishes in thickness.

In the case, therefore, of material such as iron, if the field within the outer shell is such that the permeability of the outer shell is the greater (which will generally be the case when the enclosed space is protected), it will be better to make the external shell relatively thicker than the above calculation would indicate. Conversely, if the inner shell has the higher permeability its thickness should be increased.

There is no difficulty in eliminating α_1 and α_2 in turn from the relations obtained by equating the coefficients of $d\alpha_1$ and $d\alpha_2$ in (32) to zero, and thus finding the best values in any given case for which the equations can be solved by trial.

Summary.

In conclusion it is perhaps desirable to summarize the principal results of the foregoing discussion. In doing so I shall confine myself exclusively to the corresponding cases of a small magnet placed in the centre of the shells, and of shells placed in a uniform field, and thus the interpretation of the symbols is valid for these cases only.

The results depend upon two quantities, viz., the ratio of the outermost to the innermost radius of the series of shells.

In the paper the cube of this quantity is indicated by the symbol $L = \alpha_0/\alpha_n = a_n^3/a_0^3$, where n refers to the outermost surface.

The other quantity ϵ is a function of the permeability. In the cases which I am now considering,

$$\epsilon = \frac{9\mu}{(2\mu+1)(\mu+2)} = \frac{9}{2\mu} \text{ approximately,}$$

when μ is large.

If we suppose the innermost radius of the shells (a_0) to be fixed, and the thickness of the space utilized for shielding to increase gradually from zero to a thickness t, the material employed is most efficient if fashioned in the form of a single shell until

$$\frac{t}{a_0} = (1+\epsilon)^{\frac{1}{3}} - 1 = \frac{3}{2\mu} \text{ approximately,}$$

if μ is large.

After that the material will be better employed if we divide it into separated shells; but the result obtained by the best use of the given quantity of material can be still further improved by filling up the space between the shells with more of the material, provided the thickness of the whole shell occupied by the shielding machinery is less than the value given by

$$\frac{t}{a_0} = (1 + \sqrt{\epsilon})^{\frac{2}{3}} - 1 = \sqrt{\frac{2}{\mu}},$$

if μ is large.

After this limit is passed it becomes positively injurious to fill the whole of the shielding space with the permeable material.

Better results can always be obtained by two shells with the same internal and external radii.

If the ratio of these radii $(a_3/a_0 = \sqrt[3]{L})$ is given, the best arrangement of two shells is defined by the equations

$$\frac{a_3}{a_2} = \frac{a_1}{a_0} = \lambda^{\frac{1}{3}},$$

where λ is given by the equation

$$\lambda^3(\lambda-1) - L(\lambda-1+\epsilon) = 0.$$

The best arrangement for three shells, if the ratio of the

innermost and outermost radii is given $(a_5/a_0 = \sqrt[3]{\overline{L}})$, is defined by the equations:

$$\frac{a_5}{a_4} = \frac{a_1}{a_0} = \lambda^{\frac{1}{3}},$$

$$\frac{a_4}{a_3} = \frac{a_3}{a_2} = \frac{a_2}{a_1} = L^{\frac{1}{3}}\lambda^{-\frac{2}{3}},$$

where λ is defined by the equation

$$\lambda^{\frac{5}{3}}(\lambda - 1) - L^{\frac{1}{3}}(\lambda - 1 + \epsilon) = 0.$$

In both cases, when the permeability is great the best arrangement is that in which the radii of the successive bounding surfaces of the shells are in Geometrical Progression.

The ratio of the shielded to the unshielded field when the best arrangement is adopted is

$$\frac{L^2\epsilon^2}{(\lambda - 1)^2\{\lambda^4 - L(1 - \epsilon)\}} \quad \text{and} \quad \frac{L^{\frac{4}{3}}\epsilon^3}{(\lambda - 1)^4\{\lambda^{\frac{8}{3}} - L^{\frac{1}{3}}(1 - \epsilon)\}}$$

for two and three shells respectively, λ being in each case determined from the equation given above as appropriate to that case.

When the permeability is great and the shells are not very thin, these expressions become

$$\frac{L\epsilon^2}{(\sqrt[3]{\overline{L}} - 1)^3} \quad \text{and} \quad \frac{L\epsilon^3}{(\sqrt[5]{\overline{L}} - 1)^5} \text{ respectively.}$$

The conditions for the best arrangement in the form of two shells, when (1) the innermost radius and the total volume of the permeable material, and (2) the innermost and outermost radii and the total volume of permeable material are given, are less symmetrical but are set forth above.

In any case of an arrangement in the form of two shells of materials of different permeability, in order to obtain the best result, the thickness of the shell formed of the more permeable material should be greater, and that of the shell of less permeable material should be less than is given by the above rules.

The equations are obtained by which the best arrangement can be calculated, if the permeabilities and external and internal radii are given.

VIII. *Hysteresis attending the Change of Length by Magnetization in Nickel and Iron. By* H. NAGAOKA, *Rigakushi* [*].

[Plates I. & II.]

SINCE Joule's discovery [†] that the length of iron is changed by magnetization, the subject has been studied by Mayer [‡], Barrett [§], Bidwell [||], and Berget [¶]. Bidwell carried the investigation into very strong magnetizing fields, and discovered several new facts concerning the changes of length in ferromagnetic substances. So far, however, nothing has been definitely established regarding the manner in which these substances change length during cyclic changes of magnetization. The object of the present investigation is to ascertain if there is any hysteresis in the changes of length during magnetic cycles, and at the same time to determine its amount.

Several fruitless attempts were made before I obtained any definite result. The first method I had recourse to was that of interference-fringes. A small brass plate was brazed to the end of an iron wire, and a plane glass plate placed upon it. Separated by a thin air-film was a plano-convex lens of about 40 centim. focal length, with 23 fine dots on its plane face. The lens rested on a tripod. These different pieces of apparatus were detached from Fizeau's dilatometer. The change of length was determined by observing the displacement of the fringes produced by sodium-light. From the position of the dots it was possible to determine a change amounting almost to a hundredth part of a sodium wavelength D. But as each observation of the fringes required a few minutes, it was difficult to keep the temperature constant; and, moreover, owing to the uniformity of distribution of the fringes, it was not always easy to count the number displaced. Consequently it was necessary to devise a more delicate method, and, if possible, some means of compensating for temperature-effects.

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[*] Communicated by Prof. C. G. Knott, D.Sc., F.R.S.E.
[†] Reprint of Papers, vol. i. p. 235.
[‡] Phil. Mag. [4] xlvi. p. 177.
[§] ' Nature,' 1882.
[||] Proc. Roy. Soc. 1886 ; Phil. Trans. 1888 ; Proc. Roy. Soc. 1890.
[¶] *Compt. Rend.* tom. cxv. p. 722.

I also tried an experiment with a system of levers; but it did not work smoothly, so that the readings were capricious and could not be trusted.

These faults were, to a great extent, removed by the apparatus which I describe below. The horizontal and vertical projections of the apparatus are represented in fig. 1 and fig. 2 (Plate I.) respectively. The essential part consists of a stout brass bar 53 centim. long, 1 centim. broad, and 1·1 centim. high. It is provided with three levelling-screws (l_1, l_2, l_3). A carefully polished V-groove is cut along the bar. A small rectangular brass pillar (p) is erected at one corner of the bar. A small vertical V-groove is cut on it, and on this two points of the lever rest. The lever with a mirror attached is shown in fig. 3, both from the front and from behind. It is a small rectangular piece of brass with three steel points (p_1, p_2, p_3), of which two (p_1, p_2) rest on the V-groove in p. The other point (p_3) comes in contact with a small plane glass plate, which is fixed to the end of the movable brass rod. The point of contact is in the prolonged axis of the wire whose change of length is to be determined. The distance of the line $p_1 p_2$ from p_3 is 1·125 millim. Preliminary testing showed that the relative positions of these three fine steel points were not directly affected by the magnetizing forces. The plate has three holes (h_1, h_2, h_3). To the holes $h_2 h_3$ is attached a thin brass wire, which is pulled at its middle by means of a small spiral spring (s_2) of hard brass wire. Another spring (s_1), similarly made, is attached to the other hole. These springs can be adjusted by means of slide arrangements, n_1 and n_2, attached to the sides of the bar. The circular mirror, m, attached to the lever was obtained from Hartmann and Braun.

The greatest difficulty in the measurement of change of length by magnetization arises from the temperature-changes produced by a current passing into the magnetizing coil. On this account most experimenters have passed the current only for a very short time, and observed the change before the temperature produced any effect. The consequence is that the changes are traced only by jumps. I found that the temperature-effect could be greatly compensated for by applying the principle of the gridiron-pendulum. This end was achieved by using zinc rods of different lengths such that, in any combination, the total expansion due to small changes of temperature in particular lengths of zinc and iron (or nickel) was equal to that in a particular length of brass.

Zinc rods 5 millim. thick were carefully turned on a lathe, and cut into proper lengths.

The extremities of the zinc rod (z in fig. 1) are concave, so that the convex ends of the brass rods (a, w') come into contact at the axial points of the rod. To the ends of the wire (w) are brazed two short brass rods (w', w'), about 1 centim. long and 5 millim. thick, with their ends made convex. [In brazing the wire care was taken that the axis of the wire coincided with the axes of the rods.]

A brass rod (b), 5 millim. thick, is placed in contact with w'. At the end of the rod a plane glass plate is attached, so that the steel point p_3 of the lever comes in contact with it. At the other extremity of the row of rods is a stop. It consists of a triangular prism of brass to which a brass rod (d), 5 millim. thick, is attached. The prism fits in the V-groove, and is fixed tightly by means of a clamping-screw, c. To adjust the length (b c) it is provided with a slit g. The screw (c) can be placed at any part of the slit, and the position of the movable system b, w', w, w', z, can be so adjusted that the plane of the lever is perpendicular to the axis of the system. The slight push exerted by the springs (s_1, s_2) on the movable system prevents the play of different parts among each other, and was sufficient to overcome friction during contraction.

Perhaps the following short explanation of figs. 1 and 2 will make the various parts of the apparatus clear :—l_1, l_2, l_3, levelling-screws ; a, lever with three steel points (dots in the figure) ; p, pillar with vertical groove ; s_1, s_2, brass springs attached to the lever for adjustment ; n_1, n_2, slide arrangement for adjusting the strength of the springs ; k_1 k_2, k_3 k_4, clamping-screws for n_1, n_2 respectively ; b, brass rod with plane glass ; w', w', brass rods attached to the extremities of the wire w ; w, wire whose change of length is to be measured ; z, compensating zinc rod ; d, brass rod attached to the stop ; g, slit in the stop ; c, clamping-screw.

The rod was placed inside a solenoid 30 centim. long, which lay in a horizontal position magnetic east and west. It had a resistance of 0·63 ohm, and gave a field of 37·97 C.G.S. units for a current of one ampere. The internal diameter of the solenoid was 3·0 centim., and no part of the measuring apparatus came in contact with it. Care was taken to place the apparatus along the axis of the solenoid, and so to place the wire that its middle point coincided with that of the solenoid. These precautions were always necessary, especially when the wire was thick.

The optical method for observing the change of angle requires little explanation. When the Gauss-Poggendorff method is used at a great distance, it requires very strong illumination of the scale and a good observing-telescope ; or when the reflected spot of light is read on the scale, electric- or lime-light must be used. This inconvenience can be removed in the following manner (see fig. 4).

A fine glass thread t is placed vertically in the focus of a small achromatic lens c, and illuminated by a lamp. The ray, after passing the lens, is reflected by a right-angled prism p, and thrown on the mirror m. After reflexion in the plane mirror, the ray traverses an achromatic lens L (whose focal length was about 70 centim. in my experiment). The image of the glass thread is then observed by means of a microscope, M, provided with a micrometer. I used a micro-scope detached from a geodetic comparator ; the magnifying-power was about 40, but if great exactness be desired it can be increased about five times, provided sufficient illumina-tion be given. In place of the glass thread at t I tried a fine slit, spider or silk thread, and diamond traces on glass ; but it was found best to use a glass thread of such thickness that its image was a little greater than the movable double threads of the micrometer. In the present experiment, 1776 divisions of the micrometer were equal to $524''\cdot1$, so that a single division was equal to $0''\cdot295$. The displacement of one micrometer division, therefore, gave a change of length

$$= \frac{0\cdot1125 \times 0\cdot295 \times 4\cdot848 \times 10^{-6}}{2} \text{ centim.}$$

$$= 0\cdot805 \times 10^{-7} \text{ centim.} = 0\cdot00137\,\lambda_D,$$

where λ_D represents the wave-length of the sodium-line D.

In experiments with the nickel wire through wide ranges of magnetizing force, the contraction was so great that the image of the thread passed out of the field of the microscope. The lens and microscope were then replaced by a telescope, in the focus of which was placed a scale divided to tenths of a millimetre ; a single division corresponded to $20\cdot2 \times 10^{-6}$ centim. It is easy to see that the collimating-lens c can be replaced by the lens L. For this, it is necessary to place the prism between M and L, and the thread t at such a distance that the optical path through the prism to the lens is equal to its focal length. This method of measuring small

changes of angle can be advantageously used in various other researches *.

The magnetizing current was supplied by Bunsen cells, and its strength was measured by a Thomson Graded Galvanometer. The galvanometer was gauged by means of a deciampere balance. The current was always changed continuously by means of a liquid slide included in the circuit.

A rough plan of the arrangement of the different parts is given in fig. 4.

The hysteresis accompanying the change of length in nickel is not so complicated as in iron. I will first describe a few experiments made with the former metal. A nickel wire, 19·4 centim. long and 2·04 millim. thick, was carefully annealed by placing it due magnetic east and west in a porcelain tube, and heating it red-hot in a charcoal fire. The wire was then placed in the V-groove of the apparatus, and inserted in the solenoid. The strength of the current was gradually increased, and, at convenient intervals, the corresponding readings of the micrometer and galvanometer were noted, till the magnetic field was 10·2 C.G.S. units. The contraction of the wire was at first very slow, but when the field was about 8 the rate of change was greatly increased. As the field was diminished the wire tended to return to its former state, but not by its former course. There was lagging, so that the wire, for the same strength of field, was more contracted than when the field was on the increase. In fact, when the field was diminished to zero, the wire still remained contracted $38·2 \times 10^{-8}$ of its original length. When the current was reversed, the wire continued in its tendency to recover its former length until the reversed field became equal to 5. There the recovery stopped, and the wire began once more to contract, and the contracted length in field $-10·1$ was nearly the same as that in field $+10·2$. On decrease of current, the same succession of changes took place. The changes are graphically represented in fig. 5 (Pl. I.), where the course is in the order of the letters of the alphabet. The curve *c d e f g h* of a cycle from the highest field and back to it is nearly symmetrical with respect to the line of zero field, forming complete loops on both sides. The measurements are given in Table I. at the end of the paper.

On reannealing and experimenting between fields $\pm$ 30,

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* I found lately that it is more advantageous to replace the prism *p* and the mirror *m* by a small rectangular prism attached at *m*. The positions of telescopes and collimators must be suitably changed.

we get a similar curve of hysteresis (fig. 6, Pl. I). The only difference between the two is that the field which gives the minimum contraction is higher in the second case.

With still greater range of the magnetizing field very similar results are obtained, as shown by the curves (figs. 6 and 7, Pl. I.). An examination of these curves will illustrate the character of the hysteresis better than a mere verbal description.

The contraction of the magnetized nickel wire does not show any maximum so far as the experiment goes, but the curves have two points of inflexion, one in weak and the other in tolerably large fields. The measured changes of length are nearly the same as those given by Bidwell*. (See Table II. at the end of the paper.)

Before entering into the description of the hysteresis observed in iron, I will describe a few experiments on the changes observed in iron wires of different lengths. The curves A, B, C (fig. 1, Pl. II.) represent the elongations observed in iron wires whose lengths were 66, 22, and 10·6 times the diameter respectively. In the longest, the elongation reaches a maximum in field 70 nearly, and shows an inflexion-point before reaching the maximum. In curves B and C the inflexion-point has not been reached. On continuing the curve B (given in fig. 3, Pl. II.), the maximum is found in field 230, which is very large compared to the former. This relation of the elongation to the length of the magnet is very analogous to the well-known relation of magnetization to length.

The changes wrought by a cycle of magnetization on the length of iron wire is so complex as to require a detailed description. An experiment made on a wire 19·4 centim. long and 2·83 millim. thick will illustrate the nature of the hysteresis. (For measurements, see Table III.) The curve given in fig. 2 (Pl. II.) shows that the elongation in weak fields increases gradually, but that, beyond a certain strength of field, it increases rapidly until it reaches the "wendepunkt." The rate of change then gradually lessens, and the elongation reaches a maximum in field 70. Beyond this point, in increasing fields, the elongation diminishes steadily. The curve thus traced up to field 305 is *a b c d*. With decreasing current the wire again elongates, but shows lagging, so that the length of the wire for the same strength of field is shorter on the return journey until field 120 is reached. Here the branches of the curve cross. In lower fields accordingly the

* Proc. Roy. Soc. 1890.

elongation is greater in the descending than in the ascending curve, until field 25 is reached. At this point the wire begins to shorten véry abruptly. In zero field the wire is, nevertheless, longer than at the first maximum. When the field is reversed, the length continues to decrease, but only slightly, until field −15 is reached. Here the minimum occurs, and the wire begins again to lengthen. The rate of increase is comparatively slow, and reaches a maximum in field −70. Beyond this the wire shortens quite rapidly, and nearly in the same way as in ascending positive fields. With decreasing magnetizing current, the wire again shows hysteresis and the part *l m* goes below *k l.* The two branches cross in field −110, and the wire goes on elongating till it reaches a maximum at *p* in field −25. The course of changes from *l* till the field reaches its former maximum value is nearly similar to the curve *d e f g h k l*, as will be seen from inspection of the curve *l m p q r s t* (the return curve beyond *q* is given in dotted lines to avoid confusion). Although the curve of hysteresis during a magnetic cycle is very complex,[*] it is symmetrical with respect to the line of no magnetizing force. It is evident that the maximum and minimum points in the curve are due to the lagging of the maximum elongation.

The measured elongations of the wire are nearly the same as those given by Bidwell. The field at which the wire recovers its original length will probably be about 400. On extrapolating from the curves given by Bidwell [*], I find that when the wire has no longitudinal stress it will show no elongation at about the same strength of the magnetizing force.

The course of the curve is somewhat changed when the limiting field is only a little greater than that of maximum elongation. This case is elucidated in fig. 3 (Pl. II.), from an experiment made on a wire 10·5 centim. long and 4·75 millim. thick. On account of the shortness of the wire compared to its thickness, the first maximum is only reached in field 230 approximately, and, moreover, the slope of the curve in higher fields is very gradual. After describing the curve *a b c d*, the curve *d e f g h k l m n p q r s* is traced during a cycle. The peculiarity observed in this case is that in place of having the maxima as in fig. 2, there are curious "humps" in the curve at *f* and *n*. Had the magnetizing current been sufficiently strong to cause a large decrease of elongation, the

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[*] *Loc. cit.*

maxima would probably have been produced at or near these places. (For measurements see Table IV.)

Fig. 4 (Pl. II.) represents double magnetic cycles made on a wire 14·2 centim. long and 2·83 millim. thick. When the maximum elongation was reached in field 75 (which is slightly greater than in fig. 2, because the wire is shorter), the magnetizing force was decreased and a cycle performed. The cyclic curve is *b c d e f g h*. The curve evidently shows hysteresis, and is symmetrical with respect to the vertical axis. When this cycle was completed, the field was further increased till a sufficient decrease of elongation set in, and a second cycle with greater range was gone through. The curve (shown in dots) is *d' e' f' g' h' k' m' n' p' q' r' s' t' u'*, and is in every respect similar to that given in fig. 2

The experiments above described prove that elongation in iron and contraction in nickel by magnetization both show decided hysteresis. The curve of hysteresis is symmetrical with respect to the line of zero magnetizing force, so that the elongation or contraction during cyclic changes is an even function of the magnetizing force. When the wire is magnetized, it cannot be brought to its original length by simple reversal of field. While this paper was passing through the press, Mr. Lochner published the results of his investigation on the change of length in soft iron by magnetism, in the December number of this Magazine. The curve given in fig. 3 of his paper distinctly shows hysteresis.

Some of the elongations measured in nickel and iron wires are given in the following Tables.

TABLE I.—Nickel wire : $l = 19·4$ centim., $d = 2·04$ millim.

H.	$-\dfrac{\delta l}{l} \times 10^8$.	H.	$-\dfrac{\delta l}{l} \times 10^8$.	H.	$-\dfrac{\delta l}{l} \times 10^8$
0	0	3·6	43·6	− 3·8	44·3
2·0	1·2	2·2	41·5	− 2·4	42·0
2·8	1·7	0	38·2	0	36·8
3·6	2·5	− 1·8	34·1	1·6	32·7
4·7	3·3	− 2·6	30·3	3·3	29·9
6·6	4·2	− 4·5	27·8	4·1	27·4
8·5	14·8	− 6·7	28·7	4·6	27·8
9·2	25·4	− 7·8	32·4	5·4	28·6
10·2*	53·0	− 8·9	39·0	6·3	29·6
7·3	49·8	−10·1*	51·9	7·9	34·1
5·8	48·7	− 7·9	50·2	10·0	50·3
4·7	46·4	− 5·7	48·2	10·2	53·7

* Give maximum magnetizing field.

TABLE II.—Nickel wire : $l = 10 \cdot 0$ centim., $d = 2 \cdot 04$ millim.

H.	$-\frac{\delta l}{l} \times 10^7.$	**H.**	$-\frac{\delta l}{l} \times 10^7.$	**H.**	$-\frac{\delta l}{l} \times 10^7.$
0	0	35·2	92·8	− 46·5	113
11·2	2·0	25·6	80·8	− 37·5	101
14·6	6·1	19·5	64·7	− 30·2	89
17·8	18·2	9·0	40·4	− 22·7	74·8
22·9	30·3	0·0	24·2	− 18·0	64·6
25·6	40·4	− 7·8	14·1	− 15·1	58·6
30·3	52·5	− 11·9	12·1	− 8·8	42·4
36·7	64·6	− 16·1	20·2	0·0	24·2
44·2	80·8	− 20·1	26·2	4·9	18·2
54·4	98·9	− 24·3	42·4	12·4	18·2
68·9	123	− 29·4	58·5	15·9	22·2
82·3	139	− 37·3	70·7	18·8	26·2
102·4	158	− 42·5	84·8	21·8	38·3
118·6	168	− 49·4	98·9	25·9	46·5
139·4	182	− 57·9	111	28·8	60·5
158·2	190	− 67·8	127	35·2	70·6
171·4	196	− 80·7	144	42·2	86·8
230·6	218	− 101·4	162	49·7	103
235·8*	220	− 141·5	182	59·0	121
173·9	206	− 170·3	200	67·6	129
147·8	196	− 231·6*	220	80·2	146
117·9	182	− 160·4	204	104·8	168
89·6	164	− 125·2	188	126·3	186
71·8	146	− 90·9	166	149·9	196
56·1	125	− 77·0	150	175·0	206
45·7	109	− 58·7	127	234·7*	224
37·7	107				

* Give maximum magnetizing field.

TABLE III.—Iron wire : $l = 19 \cdot 44$ centim., $d = 2 \cdot 83$ millim.

H.	$\frac{\delta l}{l} \times 10^7.$	**H.**	$\frac{\delta l}{l} \times 10^7.$	**H.**	$\frac{\delta l}{l} \times 10^7.$
0	0	22·1	33·3	− 55·5	32·2
9·1	4·2	13·2	32·7	− 48·2	33·0
13·7	10·5	0·0	27·8	− 37·7	33·2
19·2	19·8	− 8·6	24·4	− 29·0	33·4
25·1	23·2	− 20·8	24·2	− 16·8	33·2
35·5	25·8	− 24·4	25·1	− 2·7	28·1
43·6	26·6	− 29·3	26·5	0·0	27·8
59·6	26·8	− 38·4	27·4	7·5	25·9
78·4	27·0	− 47·5	28·1	20·0	22·9
127	25·6	− 76·4	28·1	24·6	24·1
206	18·7	− 121·2	26·8	29·2	25·3
305 *	8·8	− 144·5	25·2	37·9	26·5
193	17·6	− 289	10·4	46·7	27·2
133	24·9	− 299 *	9·0	60·0	27·2
87·4	29·3	− 201	17·1	87·7	27·1
68·4	31·3	− 155	22·5	124	25·6
54·6	32·6	− 106	27·1	164	23·0
38·1	33·1	− 80	30·1	201	18·5
32·6	33·3	− 68·6	31·2	310 *	8·5

* Give maximum magnetizing field.

TABLE IV.—Iron wire : $l = 10.5$ centim., $d = 4.75$ millim.

H.	$\frac{\delta l}{l} \times 10^7$.	H.	$\frac{\delta l}{l} \times 10^7$.	H.	$\frac{\delta l}{l} \times 10^7$.
0	0	30.0	20.8	− 89.1	25.1
21.2	0	23.6	20.2	− 57.0	21.6
37.1	0.4	0.0	18.3	− 42.4	20.8
43.9	1.0	− 19.2	18.3	− 35.6	20.2
55.9	2.0	− 26.8	18.3	− 24.8	19.3
72.3	4.8	− 37.6	18.3	0.0	18.0
92.5	11.2	− 52.2	18.4	24.6	17.7
110	19.2	− 69.4	18.4	32.8	17.5
144	27.6	− 93.0	19.3	58.3	17.7
208.5	31.0	−109.2	22.3	74.1	18.0
333 *	29.8	−122.6	26.1	98.3	19.6
188.6	31.7	−145.6	28.9	118	24.4
115.2	30.3	−181	30.9	140	27.4
83.5	23.9	−343 *	29.9	159	30.0
60.6	21.5	−215	31.4	228	30.6
49.8	21.2	−110	28.7	341 *	29.2

* Give maximum magnetizing field.

TABLE V.—Iron wire : $l = 14.2$ centim., $d = 2.83$ millim.

First Cycle.					
H.	$\frac{\delta l}{l} \times 10^7$.	H.	$\frac{\delta l}{l} \times 10^7$.	H.	$\frac{\delta l}{l} \times 10^7$.
0	0	−34.1	25.4	13.0	24.2
17.7	13.5	−41.0	26.0	25.2	24.0
27.3	17.1	−47.5	26.5	31.4	24.6
32.7	20.5	−58.0	27.1	38.6	25.3
46.2	24.4	−74.8	27.7	43.9	26.0
60.2	26.5	−66.9	27.9	57.4	26.9
74.0	27.4	−51.8	27.9	62.8	27.2
56.2	27.7	−35.4	27.9	72.1	27.3
43.5	27.7	−23.9	27.9		
25.9	27.7	−20.5	27.3	Continued to second	
0.0	25.5	−15.6	26.3	cycle.	
−27.3	24.3	0	25.2		

Second Cycle.					
72.1	27.3	0	29.0	−32.7	32.3
90.0	27.2	− 9.2	27.2	−16.4	32.1
115	26.7	− 23.4	25.5	0	28.9
193	24.7	− 31.5	25.7	8.9	27.2
215	23.6	− 40.0	27.0	24.3	25.0
282	19.3	− 50.0	27.9	31.4	25.5
197	21.6	− 57.6	28.0	42.2	26.9
153	24.3	− 84.7	28.3	55.4	28.2
106	28.9	−135	27.6	66.0	28.2
79.0	30.5	−280 *	18.7	84.5	28.1
63.2	31.9	−184	22.7	89.0	28.0
40.8	32.2	−118	28.4	115	27.7
25.2	32.2	− 74	31.8	144	27.2
16.7	31.7	− 59	32.3	184	26.0
8.9	30.7	− 47	32.3	286	18.8

* Give maximum magnetizing field.

IX. *Magnetic-Elongation and Magnetic-Twist Cycles.* *By* Prof. C. G. Knott, *D.Sc., F.R.S.E.**

IN measuring the successive changes of length of iron
and nickel wires subjected to cyclic magnetizations, Mr.
Nagaoka has worked out a problem of extreme difficulty. Not
only is the quantity to be measured excessively minute, but,
unless very refined precautions are taken, it is certain to be dis-
turbed beyond recognition by inevitable temperature-changes.
With admirable experimental skill, Mr. Nagaoka has applied
the principle of the gridiron-pendulum ; and the remarkable
smoothness of the curves which embody his instructive results
is an evidence of the perfection of the compensation. Joule's
original experiments, and all similar experiments of later date,
demonstrated the existence of what might be called a residual
elongation when the magnetizing force was removed. Mr.
Nagaoka has now given us the whole history of the magnetic-
elongation cycle, and has done for this very much more
difficult enquiry what Warburg and Ewing did for the mag-
netization cycle.

It may not be without interest to compare Mr. Nagaoka's
results with what I believe to be closely related results obtained
by myself several years ago. As long ago as 1858 Wiedemann
discovered † that, when a current passes along a longitudinally
magnetized iron wire, the wire twists. In 1883 I observed
the same phenomenon with nickel wire similarly treated, and
more recently also with cobalt ‡. This phenomenon is, for
present purposes, conveniently called the Wiedemann Effect.
Maxwell suggested that it could be explained in terms of
the Joule Effect, as we may also conveniently term the
phenomenon which has been engaging Mr. Nagaoka's atten-
tion. In my papers on the subject I have brought this probable
explanation prominently forward. The general features of
the Wiedemann Effect in the three magnetic metals were
just what was to be expected if Maxwell's explanation were
admitted. Not only so, but certain of these features sug-
gested corresponding characteristics in the Joule Effect—
characteristics which Mr. Bidwell has subsequently observed §.

In my paper of 1891 (Trans. R. S. E. vol. xxxvi.) I have
given the magnetic-twist cycles both for iron and nickel.
While a steady current was passing along the wire the longi-

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* Communicated by the Author.
† See Wiedemann's *Electricität*, Bd. iii.
‡ See Trans. Roy. Soc. Edin. vols. xxxii., xxxv., and xxxvi.
§ See Proceedings Roy. Soc. vol. i. (1892), p. 495.

tudinal field acting on the wire was gradually altered between limits $\pm$ **H**, and at suitable intervals observations of the twist were made.   With small range of field the hysteresis curve obtained by plotting twist against field was very similar to the well-known hysteresis curve of magnetization.   But with limiting fields stronger than the field which produced the maximum twist, the hysteresis curve crossed itself twice and formed three loops.   A typical example is shown in the figure, the magnetic-twist cycle being the Z-shaped graph with the thick lines.
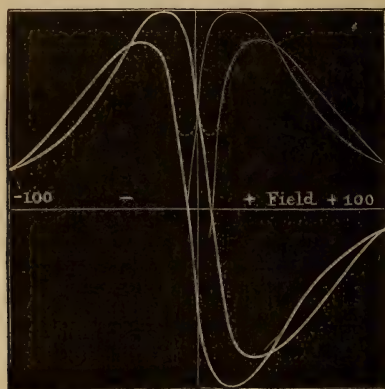
Magnetic-Twist Cycle.

In the magnetic-elongation cycle, the change of sign of the magnetizing force does not produce a change of sign in the elongation.   On the other hand, in the magnetic-twist cycle, as the magnetizing force passes through zero from positive to negative, the twist tends to do the same, though laggingly. Suppose, now, that we change the sign of the twist throughout one-half of the cycle.   In other words, take the reflexion of the one-half of the graph in the horizontal axis, as indicated by the thin lines in the figure.   Then round off the sharp angles by the dotted lines, and we get a curve similar to Mr. Nagaoka's magnetic-elongation curve, fig. 2, Plate II. Or, taking Mr. Nagaoka's curves of fig. 4, Plate II., we may reflect one half of each in the horizontal axis, join the parts so as to have continuous flowing lines, and thus get curves identical in form with those of the magnetic-twist cycle (see plate iii. of my paper already referred to).

The magnetic-elongation curves obtained for nickel are all of the simpler two-looped form, the reason being that there is no maximum contraction for nickel.   But with high ranges

of field, the magnetic-twist curve for nickel is exactly similar to the same for iron. The reason is simply that with nickel there is a field of maximum twist for each value of current passing along the wire, although there is no field of maximum elongation. The explanation of this is given in my paper of 1888 (Trans. R. S. E. vol. xxxv.). It is sufficient to note that the twist, under a given combination of circular and longitudinal magnetizing forces, depends not only upon the elongations but also upon some function of these forces which changes sign with each, and to which the existence of the maximum twist is largely or altogether due. For even in the case of iron, which has a maximum elongation, the maximum twist occurs in quite a different field. Indeed the field of maximum twist varies with the value of the current along the wire.

Meanwhile the broad character of the hysteresis in the magnetic-elongation cycle, as established by Mr. Nagaoka's delicate experiments, agrees perfectly with what might be inferred from the character of the hysteresis in the magnetic-twist cycle—a phenomenon whose experimental study is one of the simplest in the whole subject of magnetic strains.

Edinburgh University,
  October 28, 1893.

X. *On the Law of Distribution of Energy.* By S. H. BURBURY, *F.R.S.*[*]

IF there be in any space a great number of mutually acting molecules, Boltzmann's law of distribution of energy requires that the number per unit of volume of molecules whose coordinates and momenta lie between assigned limits varies as $\epsilon^{-h(\chi+\mathrm{T})}$ in the known notation. The proofs of that law given by Boltzmann and Watson are based on the hypothesis that, from the instant when mutual action commences between two molecules to the instant when it ceases, no action takes place between either of them and any third molecule, or, as it is called, the encounters are binary. I propose to consider the more general case when, for instance, no group of molecules is ever free from the action of other parts of the system.

PART I.

(1) The following is a known proposition in the theory of Least Squares.

Let the chance of a certain magnitude lying between x and $x+dx$ be $f(x)dx$, $f(x)$ being a function which vanishes

for infinite values of x, and is not altered by changing the sign of x, so that

$$\int_{-\infty}^{\infty} f(x)\, dx = 1.$$

$$\int_{-\infty}^{\infty} f(x)\, x\, dx = 0.$$

Let

$$\int_{-\infty}^{\infty} f(x)\, x^2 dx = \overline{x^2}.$$

Let there be N, a very great number, of such magnitudes, each independent of all the others, denoted by $x_1, x_2 \ldots x_N$.

Let it be required to find the chance that

$$\frac{1}{\sqrt{N}}\,(x_1 + x_2 + \ldots + x_N)$$

shall lie between c and $c + dc$, and let this chance be $F(c)dc$.

Then by the known method we find

$$F(c) = C \int_{-\infty}^{\infty} d\theta\, X^N\, \epsilon^{-c\theta\sqrt{-1}},$$

in which C is constant and

$$X = \int_{-\infty}^{\infty} dx\, f(x)\, \epsilon^{\frac{x\theta\sqrt{-1}}{\sqrt{N}}}\, dx$$

$$= \int_{-\infty}^{\infty} f(x)\, dx$$

$$+ \frac{\theta\sqrt{-1}}{\sqrt{N}} \int_{-\infty}^{\infty} x f(x)\, dx \text{ (which is zero as stated)}$$

$$- \frac{1}{N}\frac{\theta^2}{2} \int_{-\infty}^{\infty} x^2 f(x)\, dx$$

$$+ \text{ terms involving } \theta^3 \text{ \&c.}$$

$$= 1 - \frac{1}{N}\overline{x^2}\frac{\theta^2}{2} + \text{ terms involving } \theta^3 \text{ \&c.}$$

$$= \epsilon^{-\frac{1}{N}\overline{x^2}\frac{\theta^2}{2}} + \text{ terms involving } \theta^3 \text{ \&c.,}$$

and therefore

$$X^N = \epsilon^{-\overline{x^2}\frac{\theta^2}{2}} + \text{\&c.}$$

It is then shown that

$$X = 1 \text{ if } \theta = 0,$$
$$X < 1 \text{ if } \theta \neq 0;$$

and therefore in forming X^N, N being very great, we may neglect powers of θ above θ^2, and so

$$X^N = \epsilon^{-\overline{x^2}\frac{\theta^2}{2}},$$

and

$$F(c) = C \int_{-\infty}^{\infty} d\theta \, \epsilon^{-\left(\overline{x^2}\frac{\theta^2}{2} + c\theta\sqrt{-1}\right)},$$

which is proportional to

$$\epsilon^{-\frac{c^2}{2\overline{x^2}}};$$

and the constant C is found from the condition that

$$\int_{-\infty}^{\infty} F(c)\,dc = 1.$$

(2) That proposition has been extended as follows. Let $x_1, x_2 \ldots x_n$ be n mutually dependent magnitudes, and let the chance that they shall simultaneously have the values denoted by $x_1 \ldots x_1 + dx_1$, &c., be

$$f(x_1 \ldots x_n)dx_1 \ldots dx_n,$$

where $f(x_1 \ldots x_n)$ is a function which vanishes for infinite values of the variables $x_1 \ldots x_n$, and which is not altered when they all change sign together. Let us call the simultaneous occurrence of $x_1 \ldots x_n$ an *association*. The limits for each x shall be $\pm\infty$. Then we have

$$\iint \ldots f(x_1 \ldots x_n)dx_1 \ldots dx_n \quad = 1,$$
$$\iint \ldots f(x_1 \ldots x_n)x_1 dx_1 \ldots dx_n \quad = 0 \text{ \&c.}$$

Let
$$\iint \ldots f(x_1 \ldots x_n)x_1^2 dx_1 \ldots dx_n \quad = \overline{x_1^2},$$
$$\iint \ldots f(x_1 \ldots x_n)x_1 x_2 dx_1 \ldots dx_n = \overline{x_1 x_2} \text{ \&c.}$$

Let there now be N such associations, N being very large, and let each be independent of all the others. The variables in the first association shall for distinction be called x_{11}, $x_{12} \ldots x_{1n}$, those in the second association $x_{21}, x_{22} \ldots x_{2n}$, and so on to $x_{N1}, x_{N2} \ldots x_{Nn}$.

Let it now be required to find the chance that

$$x_1' = \frac{x_{11} + x_{21} + \ldots + x_{N1}}{\sqrt{N}} \text{ shall} = c_1 \ldots c_1 + dc_1,$$

$$x_2' = \frac{x_{12} + x_{22} + \ldots + x_{N2}}{\sqrt{N}} \text{ shall} = c_2 \ldots c_2 + dc_2,$$

&c.   &c.   &c.

$$x_n' = \frac{x_{1n} + x_{2n} + \ldots + x_{Nn}}{\sqrt{N}} \text{ shall} = c_n \ldots c_n + dc_n,$$

and let this chance be $F(c_1 \ldots c_n) dc_1 \ldots dc_n$.

In the same way as for one variable x we find that

$$F(c_1 \ldots c_n) = K \int_{-\infty}^{\infty} d\theta_1 \ldots \int_{-\infty}^{\infty} d\theta_n \ X^N \epsilon^{-(c_1 \theta_1 + \ldots + c_n \theta_n)\sqrt{-1}},$$

in which K is constant and

$$X = \int\int_{-\infty}^{+\infty} \ldots f(x_1 \ldots x_n) \epsilon^{\frac{1}{\sqrt{N}}(x_1 \theta_1 + \ldots + x_n \theta_n)\sqrt{-1}} dx_1 \ldots dx_n.$$

That is,

$$X = \int\int \ldots f(x_1 \ldots x_n) dx_1 \ldots dx_n$$

$$+ \frac{\theta_1 \sqrt{-1}}{\sqrt{N}} \int\int \ldots x_1 f(x_1 \ldots x_n) dx_1 \ldots dx_n + \&c.$$

$$- \frac{1}{N} \frac{\theta_1^2}{2} \quad \int\int \ldots x_1^2 f(x_1 \ldots x_n) dx_1 \ldots dx_n$$

$$- \frac{1}{N} \theta_1 \theta_2 \int\int \ldots x_1 x_2 f(x_1 \ldots x_n) dx_1 \ldots dx_n$$

$$- \&c.$$

+ terms involving powers and products of $\theta_1 \ldots \theta_n$ above the second degree.

All terms of the form $\int\int \ldots x f(x_1 \ldots x_n) dx_1 \ldots dx_n$ vanish by the conditions of $f(x_1 \ldots x_n)$.

The higher powers and products will be neglected for the same reason as in the case of one variable; and therefore

$$X = 1 - \frac{1}{N} \frac{\theta_1^2}{2} \overline{x_1^2} - \frac{1}{N} \theta_1 \theta_2 \overline{x_1 x_2} + \&c.$$

$$= \epsilon^{-\frac{1}{N}(\overline{x_1^2}\frac{\theta_1^2}{2} + \overline{x_1 x_2}\theta_1 \theta_2 + \ldots)},$$

$$X^N = \epsilon^{-(\overline{x_1^2}\frac{\theta_1^2}{2} + \overline{x_1 x_2}\theta_1 \theta_2 + \ldots)},$$

the index containing all squares and products of $\theta_1 \ldots \theta_n$; and therefore $F(c_1 \ldots c_n)$

$$= K \iint \ldots \epsilon^{-\left\{\overline{x_1}^2 \frac{\theta_1^2}{2} + \overline{x_1 x_2} \theta_1 \theta_2 + \ldots + (c_1 \theta_1 + \ldots + c_n \theta_n)\sqrt{-1}\right\}} d\theta_1 \ldots d\theta_n,$$

the limits being $\pm \infty$, and K being a constant to be found by making $\iint \ldots F(c_1 \ldots c_n) dc_1 \ldots dc_n = 1$.

(3) Now for two variables x_1, x_2 we find that

$$\int_{-\infty}^{\infty} d\theta_1 \int_{-\infty}^{\infty} d\theta_2 \, \epsilon^{-\left\{\overline{x_1}^2 \frac{\theta_1^2}{2} + \overline{x_1 x_2}\theta_1\theta_2 + \overline{x_2}^2 \frac{\theta_2^2}{2} + (c_1\theta_1 + c_2\theta_2)\sqrt{-1}\right\}}$$

$$= \frac{2\pi}{\sqrt{\overline{x_1}^2\,\overline{x_2}^2 - |\overline{x_1 x_2}|^2}} \epsilon^{-\frac{\overline{x_2}^2 \frac{c_1^2}{2} - \overline{x_1 x_2}c_1 c_2 + \overline{x_1}^2 \frac{c_2^2}{2}}{\overline{x_1}^2\,\overline{x_2}^2 - |\overline{x_1 x_2}|^2}}$$

$$= \frac{2\pi}{\sqrt{d}} \epsilon^{-\left(\frac{d_{11}}{d}\frac{c_1^2}{2} + \frac{d_{12}}{d}c_1 c_2 + \frac{d_{22}}{d}\frac{c_2^2}{2}\right)},$$

where d is the determinant,

$$d = \begin{vmatrix} \overline{x_1}^2, & \overline{x_1 x_2} \\ \overline{x_1 x_2}, & \overline{x_2}^2 \end{vmatrix}$$

and d_{11}, d_{12}, d_{22} are its minors.

We infer, and it can be proved, that the same law holds for n variables. That is that if

$$d = \begin{vmatrix} \overline{x_1}^2, & \overline{x_1 x_2}, & \ldots & \overline{x_1 x_n} \\ \overline{x_1 x_2}, & \overline{x_2}^2, & \ldots & \overline{x_2 x_n} \\ \cdot & \cdot & \cdot & \cdot \cdot \cdot \overline{x_n}^2 \end{vmatrix}$$

then

$$F(c_1 \ldots c_n) = K \frac{(2\pi)^{\frac{n}{2}}}{\sqrt{d}} \epsilon^{-\left\{\frac{d_{11}}{d}\frac{c_1^2}{2} + \frac{d_{12}}{d}c_1 c_2 + \ldots\right\}},$$

in which d_{1r} is the minor formed by omitting the first row and rth column of d, and its sign is such that

$$d = \overline{x_1}^2 d_{11} + \Sigma_{r=2}^{r=n}\overline{x_1 x_r} d_{1r}.$$

(4) Now there exists a determinant

$$D = \begin{vmatrix} 2a_1, & b_{12} & \ldots & b_{1n} \\ b_{12}, & 2a_2 & \ldots & b_{2n} \\ \cdot & \cdot & \cdot & \cdot \cdot 2a_n \end{vmatrix}$$

such that

$$\overline{x_1}^2 = \frac{D_{11}}{D}, \quad \overline{x_1 x_2} = \frac{D_{12}}{D}, \text{ &c.,}$$

and therefore

$$d = \Sigma \pm \frac{D_{11}}{D} \quad \frac{D_{22}}{D} \ldots;$$

and thence by a known proposition * we find

$$\frac{d_{11}}{d} = 2a_1, \ \frac{d_{12}}{d} = b_{12}, \text{ &c., and } D = \frac{1}{d};$$

and therefore

$$F(c_1 \ldots c_n) = K (2\pi)^{\frac{n}{2}} \sqrt{D} . \epsilon^{-(2a_1 \frac{c_1^2}{2} + b_{12} c_1 c_2 + \ldots)}$$

$$= K (2\pi)^{\frac{n}{2}} \sqrt{D} . \epsilon^{-(a_1 c_1^2 + b_{12} c_1 c_2 + \ldots)}.$$

To determine K we have

$$\iint \ldots F(c_1 \ldots c_n) \, dc_1 \ldots dc_n = 1.$$

That is, since

$$\iint \ldots \epsilon^{-(a_1 c_1^2 + b_{12} c_1 c_2 + \ldots)} \, dc_1 \ldots dc_n = \frac{(2\pi)^{\frac{n}{2}}}{\sqrt{D}},$$

$$K = \frac{1}{(2\pi)^n},$$

and

$$F(c_1 \ldots c_n) = \frac{1}{(2\pi)^{\frac{n}{2}}} \sqrt{D} . \epsilon^{-(a_1 c_1^2 + b_{12} c_1 c_2 + \ldots)}.$$

(5) Again,

$$\overline{c_1^2} = \frac{1}{(2\pi)^{\frac{n}{2}}} \sqrt{D} \iint \ldots \epsilon^{-(a_1 c_1^2 + b_{12} c_1 c_2 + \ldots)} c_1^2 dc_1 \ldots dc_n$$

$$= \frac{D_{11}}{D} = \overline{x_1^2} \text{ by hypothesis.}$$

Similarly,

$$\overline{c_1 c_2} = \overline{x_1 x_2}, \text{ &c. ;}$$

and therefore

$$\overline{S}_c = \overline{S}_x ;$$

and these results are true whatever be the form of the function $f(x_1 \ldots x_n)$.

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* Todhunter, Theory of Equations, 2nd edition, p. 393.

If, further,

$$f(x_1 \ldots x_n) = \frac{\sqrt{D}}{(2\pi)^{\frac{n}{2}}} \epsilon^{-(a_1 x_1^2 + b_{12} x_1 x_2 + \ldots)},$$

we see that

$$F(c_1 \ldots c_n) = f(c_1 \ldots c_n).$$

Now let us write

$$x_1' = \frac{x_{11} + x_{21} + \ldots + x_{N1}}{\sqrt{N}},$$

$$x_2' = \frac{x_{12} + x_{22} + \ldots + x_{N2}}{\sqrt{N}}, \text{ &c.}$$

Also

$$S_1 = a_1 x_{11}^2 + b_{12} x_{11} x_{12} + \ldots$$
$$S_2 = a_1 x_{21}^2 + b_{12} x_{21} x_{22} + \ldots$$
$$\text{&c.} = \text{&c.}$$
$$S' = a_1 x_1'^2 + b_{12} x_1' x_2'.$$

Therefore expanding $x_1'^2$ &c.,

$$S' = \frac{S_1 + S_2 + \ldots + S_N}{N} + \text{terms containing products of}$$

the form $x_{1p} x_{2q}$, that is products of two x's taken from different associations, which terms are not generally zero.

(6) The truth of the foregoing propositions will not be affected if for a_1, b_{12}, &c. we write κa_1, κb_{12}, &c., where κ is any positive constant. In this case D becomes $\kappa^n D$ and S becomes κS. It will be convenient if at this point we introduce a factor corresponding to Boltzmann's h, namely, $\frac{n}{2T}$, so that henceforth we will write

$$S = a_1 x_1^2 + b_{12} x_1 x_2 + \text{ &c.,}$$
$$F(x_1 \ldots x_n) = C\epsilon^{-\frac{nS}{2T}},$$

where

$$C = \frac{\sqrt{D}}{(2\pi)^{\frac{n}{2}}} \left(\frac{n}{2T}\right)^{\frac{n}{2}}$$

and

$$D = \Sigma \pm 2a_1 2a_2 \text{ &c.}$$

In this case also

$$\overline{x_1^2} = \frac{2T}{n} \frac{D_{11}}{D}, \quad \overline{x_1 x_2} = \frac{2T}{n} \frac{D_{12}}{D}, \text{ &c.,}$$

and

$$\overline{S} = C \iint \cdots \epsilon^{-\frac{nS}{2T}} S \, dx_1 \cdots dx_n$$

$$= \frac{2T}{n} \left\{ a_1 \frac{D_{11}}{D} + b_{12} \frac{D_{12}}{D} + \cdots \right\} = \frac{2T}{n} \frac{n}{2} = T,$$

because

$$a_1 D_{11} + b_{12} D_{12} + \cdots = \frac{n}{2} D.$$

(7) We have assumed that the quadratic function

$$S = a_1 x_1^2 + b_{12} x_1 x_2 + \&c.$$

must have its coefficients so chosen as that it shall be positive for all values of the variables $x_1 \ldots x_n$. The condition that this may be the case is that the determinant

$$D = \begin{vmatrix} 2a_1 & b_{12} \ldots b_{1n} \\ b_{12} & 2a_2 \ldots \\ \cdots \cdots & 2a_n \end{vmatrix}$$

and all its coaxial minors shall be positive. Hence each of the coefficients a is positive, and $4a_p a_q - b_{pq}^2$ is positive for all values of p and q.

If S be the energy of an association, the above condition is necessary for its *stability*. So for two associations near to one another, let the energy be $a_1 x_1^2 + b_{12} x_1 x_2 + \cdots + a_1' x_1'^2 + \&c.$, and let Δ be the double determinant $\Sigma \pm 2a_1, 2a_2 \ldots 2a_1' \ldots$. Then in order that the two associations, considered as a single system, may be stable, Δ and all its coaxial minors must be positive. If the expression for the energy contains no terms of the form bxx', where x belongs to one and x' to the other association, Δ is the product of the two single determinants $\Sigma \pm 2a_1, 2a_2 \ldots$ and $\Sigma \pm 2a_1', 2a_2' \ldots$, and if the condition be satisfied for them, it is satisfied for Δ. But if any terms of the form bxx' make their appearance, they may make Δ or some of its coaxial minors negative, and the two associations, though separately stable, may be unstable together, and dissociation may ensue.

PART II.

(8) Now let us suppose that S is proportional to the kinetic energy, or to a part of the energy, of an association. Let the number of associations, or, as we will now call them, systems, be very great. Each has its own S. And we will effect a

redistribution of S among them in the following way. Consider any group of N systems for which the variables are x_{11}, x_{21}, &c., and for which S has the values S_1, $S_2 \ldots S_N$. Let these contribute respectively $\dfrac{S_1}{N}$, $\dfrac{S_2}{N}$, &c.; and let the contribution $\dfrac{S_1}{N}$ be represented by the energy of a similar system whose variables are $\dfrac{x_{11}}{\sqrt{N}}$, $\dfrac{x_{12}}{\sqrt{N}}$, &c.; and let $\dfrac{S_2}{N}$ &c. be represented in the same way.

From that group of N systems we will form the variables $x_1' \ldots x_n'$ for one system in the new distribution by making

$$x_1' = \frac{x_{11} + x_{21} + \ldots + x_{N1}}{\sqrt{N}},$$

$$x_2' = \frac{x_{12} + x_{22} + \ldots + x_{N2}}{\sqrt{N}},$$

&c. &c.

see *post.* (11).

Now let us take at random other groups, each of N systems, and deal with them in the same way. And so on until every original system has appeared N times as a member of a group of N. Since in case of each group it loses $\dfrac{S}{N}$, it will finally have parted with all its energy S. When this process has been carried out, the whole of S for all the systems will have been redistributed among them. And owing to the mode of formation of x_1' &c., the chance of the variables $x_1' \ldots x_n'$ of any system in the new distribution having the values $c_1 \ldots c_1 + dc_1$ &c. is $C\epsilon^{-\frac{nS}{2T}} dc_1 \ldots dc_n$, and the aggregate energy will not have been altered.

(9) If, then, for the original systems

$$f(x_1 \ldots x_n) = C\epsilon^{-\frac{nS}{2T}},$$

the law of distribution is the same for the new as for the original system. In other words, it is unaffected by our process of redistribution.

If for the original systems $f(x_1 \ldots x_n)$ have any other form, we shall choose a_1, b_{12}, &c., to satisfy the equations

$$\overline{x_1^2} = \frac{D_{11}}{D}, \quad \overline{x_1 x_2} = \frac{D_{12}}{D}, \text{ &c.,}$$

where D is the determinant of $\frac{n}{2T} 2a_1$, $\frac{n}{2T} b_{12}$, &c., and then

in the redistributed system the law will be

$$F\left(c_1 \ldots c_n\right) = C\epsilon^{-\frac{nS}{2T}},$$

as before, and will remain unaffected by any further redistribution. In stationary motion, therefore, $F\left(c_1 \ldots c_n\right)$ has the

form $C\epsilon^{-\frac{nS}{2T}}$, with a quadratic function for S, whether the initial distribution $f\left(x_1 \ldots x_n\right)$ has that form or not.

This assumes that the process of redistribution of the original systems has been carried out completely. If it be carried out only partially, as for instance if only a portion of the original systems be subjected to the process, the distribution in the new system will approximate more and more to

the permanent form $C\epsilon^{-\frac{nS}{2T}}$, according as the redistribution is more complete. And by successive partial redistributions it will ultimately be reduced to the permanent or stationary form.

(10) The processes which we have supposed to take place successively may, of course, take place simultaneously. Further, we may suppose the whole process of redistribution to take place at a given rate per unit of time. Finally, our results will not be affected if the variables in any association undergo any other series of changes during the same time, provided these changes do not on average alter S.

(11) By the method of art. 8 energy is conserved in the final result, but is not conserved in each separate process, because generally S′, the energy which we suppose to be received by a system in the new distribution, is not equal to $\frac{S_1 + S_2 + \ldots + S_N}{N}$, the energy which the contributing systems

part with. That may create a difficulty in the application of the method to a physical system, even although, when the contributing systems are rapidly oscillating and in different

phases, it may be that $S' = \frac{S_1 + S_2 + \ldots + S_N}{N}$ on the average

of a very short time.

(12) If our associations be material systems fixed in space, we may suppose the energy, S, of oscillation to be transmitted through space—*i. e.* æther—in waves with conservation of energy, so that the energy of a wave which passes per unit area and time through a spherical surface of radius R

described about the centre of disturbance varies as $\frac{1}{4\pi R^2}$, or varies as $\frac{1}{N}$, if $N = 4\pi R^2$ and the coordinates x, of which that energy is a quadratic function, vary as $\frac{1}{\sqrt{N}}$. If, now, we may further assume that any number of such waves may coexist, so that the disturbance x at any point at any instant is the algebraic sum of the disturbances due to all the waves which are passing the point at that instant, the redistribution of S will go on in the physical system in exactly the same way as in our analytical system—and with the same result, that the distribution denoted by $C\epsilon^{-\frac{nS}{2T}}$ will be permanent. The disturbances $x_1 \ldots x_n$ in any system will be respectively $\frac{1}{2R\sqrt{\pi}}$ times the sums of the values of the corresponding disturbances in systems distant R from the one in question, as they were t seconds ago, $\frac{R}{t}$ being the velocity of wave-motion. The potential energy, χ, of the internal forces of a system we suppose not to be capable of transmission in that form. But if the law of distribution be $\epsilon^{-h(\chi+S)}$, we know that this distribution will not be affected by the internal forces; neither will it be affected, on the above hypothesis, by the transmission of S. It will therefore be permanent.

But if we are not allowed to assume the coexistence of waves in the sense above stated, the law cannot be permanent, except in the known case of binary encounters.

Part III.

(13) Our investigation hitherto has been based on the assumption that the N associations are *independent* of one another; that is, that the chance of the variables $x_1 \ldots x_n$ in one association having assigned values is independent of the values of $x_1' \ldots x_n'$ the variables in another association, or, if $f(x)$ be the chance of any one of the first set having assigned value, $\frac{df(x)}{dx'} = 0$ for each x'. The condition of complete independence is that the expression for the energy contains no term of the form bxx', where x and x' belong to different associations. This condition may not be satisfied if our associations are material systems very near to one another.

It is necessary to replace the stringent condition by one which can be satisfied more easily, as follows:—In the first place it will be shown that our method is applicable even

when the associations are not all independent of each other, provided we can choose in many ways a group of them containing a great number which are independent of each other.

Let there be Nq systems, where N is very large and q a positive integer to which we may assign any value. Let them be called $A_1, A_2 \ldots A_{Nq}$. If it be not true that every one of the Nq systems is independent of every other, nevertheless it may be true, and we will assume that it is true, that the N systems A_1, A_{1+q}, A_{1+2q}, &c. are independent of each other. And, similarly, the N systems A_2, A_{2+q}, &c. may be independent of each other, and so on for other groups. On this assumption that A_1, A_{1+q}, &c. are mutually independent, we may apply our method to them. And let $F_1(c_1 \ldots c_n)$ $dc_1 \ldots dc_n$ be the chance that the sum of the x_1's in these N systems, each divided by $\sqrt{N}$, shall be $c_1 \ldots c_1 + dc_1$, &c.

Then $F(c_1 \ldots c_n) = C\epsilon^{-\frac{nS}{2T}}$. Also let $F_2(c_1 \ldots c_n)$ be the corresponding chance for the group A_2, A_{2+q}, &c. All the systems being supposed similar in character, evidently

$$F_1(c_1 \ldots c_n) = F_2(c_1 \ldots c_n) = \&c.$$

But the result for any one of the groups of N systems cannot differ from that for the whole Nq systems. Whence it follows that $F(c_1 \ldots c_n)$ for the Nq systems

$$= F_1(c_1 \ldots c_n) = F_2(c_1 \ldots c_n) = \&c.$$

$$= C\epsilon^{-\frac{nS}{2T}}.$$

We are therefore at liberty to apply our method to the Nq systems, provided that, although they are not all independent of each other, yet we can divide them into groups, each of N systems, the members of which are independent of one another.

(14) Again, in order that the N systems A_1, A_{1+q}, &c. may be independent of each other, it will be sufficient if we make every variable, as x, in A_1 independent of every variable x' in A_{1+q}, &c., that is $\dfrac{df(x)}{dx'}$ must be zero or negligible.

Let us therefore consider a series of single magnitudes x_1, x_2, &c. which may be the variables in many systems of n, and let the chance of their simultaneously having assigned values be

$$C\epsilon^{-\frac{n}{2T}(a_1 x_1^2 + b_{12} x_1 x_2 + \&c.)},$$

and let it be required to find the condition that $\dfrac{df(x_1)}{dx_r}$ shall

vanish. In order to find $\dfrac{df(x_1)}{dx_r}$ we integrate according to each of the other variables between the limits $\pm\infty$. The result will be proportional to $\epsilon^{-(Ax_1^2 + Bx_1 x_r)}$, where A does not concern us, and $\dfrac{df(x_1)}{dx_r} \propto$ B, or the condition that $\dfrac{df(x_1)}{dx_r}$ shall vanish is that B$=0$. Also B$=\dfrac{\Delta_{1r}}{\Delta_{1r r 1}}$, where Δ is the determinant of r rows $\Sigma \pm 2a_1\, 2a_2 \ldots$ and $\Delta_{1r r 1}$ a coaxial minor.

(15) We have, then, to find a relation between the coefficients a_1, b_{12}, &c., which will make Δ_{1r} vanish compared with $\Delta_{1r.r1}$, without making all the coefficients b vanish which connect the variables in any one of the original associations with those in any other. That can be done in many ways. It will be sufficient to give one example. Let us suppose all the a's equal to each other, and all the b's of the form $b_{p\,\overline{p+1}}$ equal to one another, and all other b's zero.

Further, let $b_{12}=b_{23}=$ &c. $= 2a\theta$.

Then the determinant assumes the form

$$\Delta = \left| \begin{array}{cccc} 2a & b & . & . \\ b & 2a & b & . \\ . & b & 2a & b \\ . & . & b & 2a \end{array} \right|$$

and if f_r be its value for r rows, the law of formation is

$$f_r = f_{r-1} - \theta^2 f_{r-2} \quad . \quad . \quad . \quad . \quad . \quad (A)$$

Since every f is to be positive, $f_{r-1} > f_r$. Ultimately as r increases the ratio $\dfrac{f_r}{f_{r-1}}$ becomes constant. Let its constant value be λ. Then equation A gives

$$\lambda = 1 - \frac{\theta^2}{\lambda},$$

or

$$\lambda = \tfrac{1}{2} \pm \frac{\sqrt{1-4\theta^2}}{2},$$

of which the positive sign will be taken. This result shows that if f, or Δ, be always positive, θ^2 cannot be greater than $\tfrac{1}{4}$, or θ greater than $\tfrac{1}{2}$. Also if $\theta = \tfrac{1}{2}$, we easily find $\Delta = \dfrac{r+1}{2^r}(2a)^r$, and therefore

$$\Delta_{1r r 1} = \frac{r-1}{2^{r-2}}(2a)^{r-2}.$$

Again, in this case

$$\Delta_{1r} = \begin{vmatrix} b & 2a & b & . \\ . & b & 2a & b \\ . & . & b & 2a \\ . & . & . & b \end{vmatrix}$$

$$= (2a)^{r-1} \theta^{r-1} = \frac{1}{2^{r-1}} (2a)^{r-1}.$$

Therefore

$$\frac{\Delta_{1r}}{\Delta_{1r\,r1}} = \frac{a}{r-1},$$

and vanishes as r increases indefinitely.

PART IV.

Boltzmann's *Minimum Function*.

(16) We have seen that, the law of distribution being $C\epsilon^{-\frac{nS}{2T}}$,

$$\overline{x_1^2} = \frac{2T}{n} \frac{D_{11}}{D}, \quad \overline{x_1 x_2} = \frac{2T}{n} \frac{D_{12}}{D}, \&c., \quad \text{and } \overline{S} = T.$$

Let us consider a varied system in which with these same values of $\overline{x_1^2}$ $\overline{x_1 x_2}$, &c. the law of distribution is $C\epsilon^{-\frac{nS}{2T}} \overline{1+q}$, where $1+q$ is any positive function of x_1, x_2, &c., and q must satisfy the following conditions, namely :—

(1) In order that the number of systems may be the same in the varied as in the normal state,

$$\iint \ldots \epsilon^{-\frac{nS}{2T}} dx_1 \ldots dx_n = \iint \ldots \epsilon^{-\frac{nS}{2T}} \overline{1+q}\, dx_1 \ldots dx_n$$

or

$$\iint \ldots q\epsilon^{-\frac{nS}{2T}} dx_1 \ldots dx_n = 0.$$

(2) In order that the values of $\overline{x_1^2}$, $\overline{x_1 x_2}$, &c., may not be altered,

$$\iint \ldots \epsilon^{-\frac{nS}{2T}} x_1^2\, dx_1 \ldots dx_n = \iint \ldots \epsilon^{-\frac{nS}{2T}} \overline{1+q} x_1^2\, dx_1 \ldots dx$$

$$\&c. \qquad\qquad \&c.,$$

and therefore also

$$\iint \ldots \epsilon^{-\frac{nS}{2T}} S\, dx_1 \ldots dx_n = \iint \ldots \epsilon^{-\frac{nS}{2T}} \overline{1+q} S\, dx_1 \ldots dx_n.$$

These conditions being satisfied the system will, on free interchange of energy, pass out of the varied state into the normal state. And it can be now shown that the function B

$$= \iint \dots f(x_1 \dots x_n)\{\log f(x_1 \dots x_n) - 1\}dx_1 \dots dx_n$$

diminishes in the process.

For let B_0 be the value of B in the normal state, when $f(x_1 \dots x_n) = C\epsilon^{-\frac{nS}{2T}}$, B its value when

$$f(x_1 \dots x_n) = C\epsilon^{-\frac{nS}{2T}}\overline{1+q}.$$

Then $B - B_0 =$

$$C\iint \dots \epsilon^{-\frac{nS}{2T}}\overline{1+q}(\log C - \frac{nS}{2T} - 1 + \log\overline{1+q})dx_1 \dots dx_n$$

$$- C\iint \dots \epsilon^{-\frac{nS}{2T}}(\log C - \frac{nS}{2T} - 1)dx_1 \dots dx_n$$

$$= C\iint \dots \epsilon^{-\frac{nS}{2T}}\overline{1+q}\log\overline{1+q}\,dx_1 \dots dx_n$$

$$= C\iint \dots \epsilon^{-\frac{nS}{2T}}\{\overline{1+q}\log\overline{1+q} - q\}dx_1 \dots dx_n,$$

because

$$C\iint \dots \epsilon^{-\frac{nS}{2T}}q\,dx_1 \dots dx_n = 0.$$

Now since $1+q$ is positive, $\overline{1+q}\log\overline{1+q} - q$ is necessarily positive, unless $q=0$, and is then zero; $B - B_0$ is therefore positive. And given T and the coefficients a_1, b_{12}, &c., B has its least possible value when $q=0$, or $f(x_1 \dots x_n) = C\epsilon^{-\frac{nS}{2T}}$.

And this least possible or minimum value differs by a constant from $\log C$ or $\log\left\{\left(\frac{n}{2T}\right)^{\frac{n}{2}}\frac{\sqrt{D}}{(2\pi)^{\frac{n}{2}}}\right\}$.

Further, $\frac{d}{dq}(B - B_0) = \log(1+q)$, and therefore $B - B_0$ diminishes as q approaches zero.

The Second Law of Thermodynamics.

(17) In stationary motion the minimum function has the value $$B = \left(\frac{n}{2T}\right)^{\frac{n}{2}}\frac{\sqrt{D}}{(2\pi)^{\frac{n}{2}}}$$ plus a constant.

It is a function of T and the parameters a_1, b_{12}, &c., or any

parameters v_1, v_2, &c., on which a_1, b_{12}, &c., depend. The second law may from one point of view be regarded as the law of the variation of B when T and the parameters vary very slowly, so that stationary motion is always attained. On this assumption the proofs of the second law depend.

We have seen that $\overline{S} = T$ and is independent of the parameters, or $\frac{d}{dv}\overline{S} = 0$ for each v. But $\frac{d\overline{S}}{dv}$ is not generally zero. It may, therefore, be the case that work has to be done on variation of any parameter v. This work will be denoted by $-\frac{d\overline{S}}{dv}\partial v$. It will include the work done against all external forces. The energy imparted during any small variation of T and the parameters will be denoted by ∂Q. Then the second law requires that $\frac{\partial Q}{T}$ shall be a complete differential.

(18) It will be sufficient to prove the law for any parameter v on which a_1, b_{12}, &c. depend. So far as this proof is concerned, there may be many such.

We have in this case

$$\partial Q = \partial T - \frac{d\overline{S}}{dv}\partial v$$

$$= \partial T - C\partial v \iint \ldots \epsilon^{-\frac{nS}{2T}} \frac{dS}{dv} dx_1 \ldots dx_n$$

$$= \partial T - C\partial v \iint \ldots \epsilon^{-\frac{nS}{2T}} \left\{ \frac{da_1}{dv}x_1{}^2 + \frac{db_{12}}{dv}x_1 x_2 + \ldots \right\} dx_1 \ldots dx_n$$

$$= \partial T - \partial v \frac{2T}{n} \left\{ \frac{da_1}{dv}\frac{D_{11}}{D} + \frac{db_{12}}{dv}\frac{D_{12}}{D} + \ldots \right\}$$

$$= \partial T - \partial v \frac{2T}{n}\frac{1}{2} \left\{ \frac{da_1}{dv}\frac{1}{D}\frac{dD}{da_1} + \frac{db_{12}}{dv}\frac{1}{D}\frac{dD}{db_{12}} + \ldots \right\}$$

$$= \partial T - \partial v \frac{T}{n}\frac{1}{D}\frac{dD}{dv}.$$

$$\frac{\partial Q}{T} = \partial \log T - \frac{1}{n}\partial \log D.$$

Now in this case,

$$\partial B = \partial \log \left\{ \sqrt{\overline{D}} \left(\frac{n}{2T} \right)^{\frac{n}{2}} \right\};$$

$$\therefore \quad \frac{1}{n}\partial \log D = \frac{2}{n}\partial B + \partial \log T;$$

$$\therefore \quad \frac{\partial Q}{T} = -\frac{2}{n}\partial B.$$

XI. *On the Relative Strengths or "Avidities" of Weak Acids.* By John Shields, *D.Sc., Ph.D.*[*]

WHEN the sodium salt of an acid A is mixed with the equivalent quantity of another acid B, the base will in general be distributed between the two acids, and the ratio of distribution will depend on the relative strengths of the competing acids A and B.

If ξ represent that fraction of the neutral sodium salt which is decomposed on the addition of the acid B, then $1-\xi$ will represent the quantity of the original salt which remains undecomposed.

By applying Guldberg and Waage's law, after equilibrium has taken place, we get

$$c(1-\xi)^2 = c_1\xi^2,$$

or

$$\left(\frac{\xi}{1-\xi}\right)^2 = \frac{c}{c_1},$$

where c and c_1 denote the velocities of the opposed reactions.

The ratio of distribution of the base between the two acids is therefore proportional to the square root of the ratio of the coefficients of velocity,

$$\frac{\xi}{1-\xi} = \sqrt{\frac{c}{c_1}}.$$

This ratio of distribution gives us the measure of the relative strengths or, as Julius Thomsen has called it, the "avidities" of the acids for any given dilution.

As regards the measurement of the ratio of distribution, Thomsen employed a calorimetric method; but Ostwald, Gladstone, Jellet, Wiedemann, and Löwenthal and Lenssen employed various other methods, which, however, are not particularly well adapted for measuring the relative strengths of very weak acids. In the present paper I propose to show how the avidities of the weakest acids may be determined from the rate at which their salt-solutions are hydrolyzed. At this stage it will be convenient to point out that water is here regarded as a weak acid, and potash and soda as the same base since they are equally strong (*cf.* Reicher, *Annalen,* ccxxviii. p. 257).

Arrhenius (*Zeitsch. f. physikal. Chem.* v. p. 13, 1890) has shown that when two weak acids compete for the same base, the ratio of distribution is very nearly proportional to

the square roots of the electrolytic dissociation-constants. But the dissociation-constant is arrived at from the equation

$$\frac{m^2}{(1-m)v} = k,$$

in which m is the degree of electrolytic dissociation or the ratio of the molecular conductivity at any given dilution, v, to that at infinite dilution. Now, when m is very small, the above equation becomes

$$\frac{m^2}{v} = k,$$

or, when the dilution for different acids is the same,

$$\frac{m^2}{m_1{}^2} = \frac{k}{k_1};$$

i. e. the electrolytic dissociation ratios are as the square roots of the dissociation-constants, or directly as the ratios of distribution.

According to Guldberg and Waage's law (as enunciated by Julius Thomsen), the ratios of distribution are as the square roots of the velocity-constants. If we call K the velocity-constant in the hydrolysis of aqueous salt-solutions, then $\sqrt{K}$ becomes the measure of the dissociation ratio, or the relative strengths of the two weak acids are as $\sqrt{K} : \sqrt{K_1}$.

To apply this method to a few specific cases, we may obtain the necessary data in my former paper on hydrolysis in aqueous solutions of salts of strong bases with weak acids (Phil. Mag. [5] xxxv. p. 365, 1893). It was there pointed out that when potassium cyanide, for example, is dissolved in water it is partially decomposed into free acid and free base, and the following equilibrium takes place :
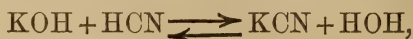
$$KOH + HCN \rightleftharpoons KCN + HOH,$$

from which we get the equation

$$KOH \times HCN = K(KCN \times HOH),$$

where $K = \dfrac{c_2}{c_1}$ of the more general equation,

$$c_1(KOH \times HCN) = c_2(KCN \times HOH),$$

in which c_1 and c_2 are the velocity-coefficients in opposite directions (Guldberg and Waage, *Journ. f. pr. Chem.* [2] xix. p. 69, 1879).

In the present case, however, we desire to study the formation of the salts or the ratio of distribution of the base

between two acids, so we may write

$$\frac{1}{K}(KOH \times HCN) = KCN \times HOH.$$

Instead of the K of the former paper we must therefore use its reciprocal $\frac{1}{K}$.

In Table I. the strengths of the acids in tenth-normal solution have been compared; that of hydrocyanic acid being arbitrarily taken as unity. The values of K are taken from the paper on hydrolysis (*loc. cit.*).

Strictly speaking only the monobasic acids are comparable; but in order to form some conception of the order of magnitude of the relative strengths of carbonic and biboric acids, the characteristic constants have been halved and the calculation proceeded with in the ordinary way.

TABLE I.

Name of acid.	K.	$\sqrt{\frac{1}{K}}$.	$\dfrac{\sqrt{\frac{1}{K}}}{28 \cdot 8}$.
Hydrocyanic acid............	1204×10^{-6}	28·8	1
Acetic acid.....................	668×10^{-10}	3869·1	134
Carbolic acid.................	925×10^{-5}	10·4	0·36
Carbonic acid	1954×10^{-5}	10·1	0·35
Biboric acid	50×10^{-5}	63·2	2·2

The great difference between acetic acid and the others is very remarkable. A still better idea of the relative strengths of these weak acids is obtained when they are compared with some of the stronger acids. Hydrochloric acid together with the three chlorinated acetic acids seem specially well adapted for this purpose, as they supply different grades of strength. The values attached to these acids are taken from Ostwald's tables, and are calculated from the velocity of catalysis of methyl acetate by half-normal solutions of the acids.

Table II. contains a list of the acids arranged in their relative order of strength.

TABLE II.

Hydrochloric acid	100
Trichloracetic acid	68
Dichloracetic acid.................	23
Monochloracetic acid	4·3
Acetic acid	0·35
Biboric acid	0·0057
Hydrocyanic acid.................	0·0026
Carbolic acid	0·00094
Carbonic acid	0·00091

The numbers attached to each acid cannot of course be considerd final. As regards carbolic and carbonic acid, for example, it is impossible to say which of the two is the stronger, all that we may safely infer is, that they are about equally strong.

From the above table it also follows that hydrochloric acid is about one hundred thousand times stronger than carbolic acid in tenth-normal solution ; or, what amounts to the same thing, the electrolytic dissociation ratio is one hundred thousand times greater in the former case than in the latter.

In other tables of the avidities of acids the values for the weakest acids are usually represented by blanks, but the method which has just been described enables us to arrange them in proper order and to assign definite values to them.

This seems all the more necessary as a great deal of misconception still prevails as to the relative strengths of the acids and the conditions under which a comparison is possible.

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XII. *Intelligence and Miscellaneous Articles.*

ON THE FREEZING-POINTS OF SODIUM-CHLORIDE SOLUTIONS.
BY S. U. PICKERING, F.R.S.

IN a recent communication to the Phil. Mag. (xxxvi. p. 484) Mr. Harry Jones has made sundry very incorrect statements as regards a controversy respecting the regularity or otherwise of the freezing-points of weak sodium-chloride solutions. I should not have troubled to correct them had Mr. Jones inserted any reference to the communication which has apparently closed this controversy (*Ber. d. deutsch. chem. Gesell.* xxvi. p. 1977), and which must have been in his hands before he corrected the proofs of his paper for this Journal.

In the *Berichte* (xxv. p. 1314) I published a series of determinations with this salt which I considered indicated the presence of

changes of curvature at certain points. Mr. Jones subsequently published (*Ber.* xxvi. p. 551) some still more accurate determinations, which he considered entirely disproved the existence of these breaks. I proved, however (*Ber.* xxvi. p. 1221), that, so far from this being the case, Mr. Jones's results showed the very same breaks as mine did, but in a still more satisfactory manner. I proved that parabolas deduced mathematically from his values so as to allow the existence of these breaks agreed most perfectly with the known experimental error as determined by two independent methods, whereas, when represented by a single parabola without breaks, the error was 10,000 times too large. Mr. Jones found it convenient to ignore the results of this investigation in his answer (*Ber.* xxvi. p. 1635), which may be summarized in his own words in the Phil. Mag. " I have carefully examined his [Pickering's] results . . . and have shown that the 'breaks' are caused only by the experimental errors in his results. Mr. Pickering has applied his method of curve-drawing to my results from sodium chloride, which differ from his to the extent of more than 50 per cent., and with it claims to have found the same 'breaks' as in his own results. He has thus shown the true value of his method, which seems to be largely independent of the experimental data. I have since shown that his curve contains the following fundamental errors :— I. At least some of the points in his curve are wrong. II. The choice of points through which he has drawn the curve is purely arbitrary."

It is true that I *did* examine Mr. Jones's results by drawing curves through them, but, as I never published the results, I fail to see how he can pretend to know anything about them, unless it is from a rough woodcut on p. 1222 of the *Berichte*. His answer, which does not, and evidently could not, apply to the mathematical investigation, appears to me to be calculated simply to shirk the results of this investigation, which are too conclusive to be withstood. His statement that my results differ from his by at least 50 per cent. may be characterized by your readers as they think fit. The sole foundation for it is that in the one extreme experiment, and in that only, there is such a difference, and that there it amounts to but $0 \cdot 002^\circ$ C., an error of which many of Mr. Jones's duplicate results are by no means innocent.

Mr. Jones's " careful examination " of my results consisted of displaying some of them in a woodcut in a manner which would inevitably fail to reveal anything as to their true nature, and his " proof " of the regularity of his own results consists of a similar plotting. I can only repeat in English what I have already told him in German (*Ber.* xxvi. p. 1979), that so long as he offers no evidence to invalidate that which I have brought forward in favour of the irregularity of these results, and so long as he declines to give the smallest proof whatever to support his statement that they form a regular curve, I must decline to discuss the matter any further.

I am tempted, however, to say a word as to Mr. Jones's recent results, although it is impossible to attempt a criticism of them till the

experimental values, instead of the present "smoothed" values, are published. The most remarkable part of the conclusions which he draws from them is that non-electrolytes in very weak solutions give an abnormally large depression similar to that given by electrolytes, but which according to the dissociation theory should be shown by electrolytes only. It is still more remarkable, however (especially when we remember that these results emanate from Prof. Ostwald's laboratory), that Mr. Jones should have published them without any reference to the fact that my own results (although they differ somewhat from his in individual cases) had established the existence of this same phenomenon, not only as regards aqueous solutions, but still more conspicuously as regards benzene solutions (*Ber.* xxiv. pp. 1469, 3329; xxv. pp. 1854, 2011, 2518, 3434).

Mr. Jones suggests a possible explanation of this excess in the case of non-electrolytes, without noticing, however, that it must apply equally to electrolytes also, and thus upset the very conclusions which he has drawn from the rest of his work, namely, that the excess is due to dissociation and agrees accurately with the electric conductivity. Perhaps I may help him a little out of his difficulty by suggesting that, after all, part of this 25 per cent. excess may be due to experimental error. When a student whose work is hitherto unknown publishes results which claim an accuracy ten times greater than any previously attained, it is but reasonable to expect fuller details than those given by Mr. Jones. A mercurial thermometer reading with certainty to the ten thousandth of a degree is an instrument unknown in England, and any systematic investigation of its capabilities would add confidence to our estimate of the results obtained. Independent of errors due directly to the thermometer, I should like to ask if Mr. Jones has satisfied himself that he gets the same value for the freezing-point of water (on which all his conclusions depend) whatever method he uses for determining it. In his apparatus the sides and bottom of the vessel are being constantly cooled by the surrounding medium, the top is being constantly heated by partial contact with the air, and the contents are being heated by the friction of the stirrer. When freezing begins, the liquid can only be kept at the same temperature as the ice if this latter is disseminated throughout it in considerable quantity and in minute particles; but, according to my experience, this is almost impossible when dealing with a large bulk of pure water, even when violently stirred: the ice forms and agglomerates on the sides of the vessel, leaving the liquid in the middle to become superheated and give too high a reading for the freezing-point. A similar phenomenon occurs to a less extent with very weak solutions, and gradually becomes negligible as the strength increases, and as the ice which separates forms in smaller crystals which do not agglomerate so easily. An error due to this cause would account for the very high values obtained by Mr. Jones for weak solutions.

XIII. *The Phases and Conditions of Chemical Change.*
By V. H. VELEY, *M.A.*[*]

> "Was nun die Beobachter einer scientifischen Methode
> betrifft, so haben sie hier die Wahl entweder dogmatisch oder
> skeptisch, in allen Fällen aber doch die Verbindlichkeit sys-
> tematisch zu verfahren."—KANT, *Kritik der reinen Vernunft.*

Introductory.

THE investigations on the subject of chemical change
published in the course of the past ten or twelve years
have more than ever rendered it difficult to give a satisfactory
answer to the questions : first, what is chemical change ?
and, secondly, what is the cause of its commencement ? It is
pretty plain, however, that in the long run these two problems
resolve themselves into the first. Recently there have arisen
two schools of thought, which, though widely opposed in
matters of detail, yet agree in the general principle that
chemical and electric phenomena are more exclusively related
to one another than to any other form of energy. On the
one hand, there are writers who hold that chemical change is
the reverse of electrolysis ; and, on the other, there are those
who consider that chemical change is conditioned by the
separation or dissociation of compounds into oppositely elec-
trified ions. Both schools have set forth answers to the

[*] Communicated by the Author.

problems of the commencement of chemical change, and especially with regard to the function and necessity of an intermediate or third substance to promote reaction between two other substances.

But generally there seems to be a tendency among writers on chemical as on other forms of philosophy to accept the hypotheses of their predecessors as matters of acquired knowledge without due examination of their validity, and to superimpose upon them other hypotheses which their successors in their turn accept as facts. In chemical philosophy, as in that of pure reason, there are writers of a dogmatic type who set forth with a most unqualified assurance hypotheses neither wholly in accordance with facts nor strictly logical in their demonstration. But others of an agnostic type are content to conceal their ignorance under such commonly accepted terms as " catalysis," " fermentation," " nascent action," and the like, which are regarded as all sufficient explanations of phenomena not understood ; such terms are of course convenient, but do not render any material assistance. Again, it is to be feared that chemists too often content themselves with a study of the ultimate products of a reaction and omit the intermediately formed substances, which, though in some cases they may be transitory, yet are the more important. It is as if the morphologist were to consider an organism as a whole, and to ignore the structure and function of individual cells, whether somatic or reproductive. In the present communication it is proposed to discuss the conditions and phases of chemical change, and to deal with the several hypotheses concerning its nature.

The Phases of Chemical Change.

From our earliest and everyday experience it is learnt that chemical changes start slowly at first, are accelerated up to a maximum and for some time constant stage, and thence, unless reversible, proceed with a velocity diminishing according to the proportion of the reacting masses. To adopt the phraseology of the biologist, the changes are at first anabolic and then katabolic. There are thus a series of phases or periods which pass into one another more or less continuously ; and though in some cases, especially of detonations and certain explosions, all these periods have not as yet been clearly defined owing to the rapidity of their succession, it is, however, reasonable to suppose that with improved methods of observation, whether of chronography or photography, these changes will be found to follow the same course.

The periods may be defined as follows :—(i.) of Commencement; (ii.) of Inertness* or Reluctance followed by Acceleration ; (iii.) of Constancy ; (iv.) of Diminution of Velocity †. The first three periods will be considered *seriatim* more fully.

(i.) *Period of Commencement.*

Writers on the kinetic theory of gases have supposed that the velocity of movement of translation of gaseous molecules is, from the nature and degree of violence of their mutual impacts, an average of velocities of widely different values ; their kinetic energy is therefore expressible by the factor $\frac{1}{2}mu^2$, wherein u is the average of velocities $V_1, V_2, \ldots V_n$. It is supposed that certain molecules will be moving with a velocity which would thereby render them more liable to atomic disruption when they meet molecules of a different kind of matter, so that the free constituent atoms which would otherwise pair with atoms of a like kind pair with atoms of an unlike kind.

Clausius further assumes that an E.M.F. (and probably changes induced by light are to be included under the same category) tends to give a "set" or direction to the atomic constituents, causing those of an electro-positive nature to pass in one, and those of an electro-negative nature to pass in another way. The same course of reasoning will apply to solutions, except that the problem is rendered more complicated by the internal viscosity of the liquid and the thereby diminished probability of molecular encounter. The theory of the free and paired atoms has been developed on mathematical lines by J. J. Thomson ‡ ; and the results calculated from the equations set forth are in agreement with those obtained in experiments on the dissociation of iodine (Crafts and Meier), of the compound of methyl oxide and hydrochloric acid (Friedel), and on the dissociation of phosphoric chloride (Wurtz).

In the particular case of hydrogen and chlorine (discussed more fully below), let us postulate the condition that certain molecules of each gas not only are moving faster, but also by the agency of light have a tendency to move in one direction

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* It seems preferable to use the term "Inertness" or "Reluctance" rather than "Inertia," as the cause is chemical rather than dynamical, and the implied analogy would therefore be misleading.

† Hell and Urech (*Ber. deut. chem. Ges.* xiii. p. 531) divide the course of chemical change into the three last periods, while Pringsheim (*Wied. Ann.* xxxii. p. 400) gives the first three, but the method of observation adopted precluded any observations of the fourth period.

‡ Phil. Mag. [5] xviii. pp. 233–268.

rather than in any other; these molecules collide, the hydrogen and chlorine atoms change partners to produce hydrochloric acid. If it be further supposed that the external temperature remains the same, and that the walls of the vessel are absolutely non-conducting, then the heat evolved by the combination of the hydrogen and chlorine would increase the velocity of translation of the remaining molecules, and thereby increase their tendency to combine, if the external cause of the " set " continued. There would thus be an acceleration of the combination up to the point at which there would be so many particles of hydrochloric acid not only in the way but also with an increasing velocity of translation. The phenomena of acceleration discussed in the succeeding section might be accounted for by dynamical considerations; but, as will be seen, this is not the conclusion of the whole matter.

However this may be, it is clear that when once a direction has been given to the molecules or their constituents whereby a chemical change is produced, they will continue to move in the same direction, and the change, other external causes not intervening, will proceed to its ultimate limit. The phenomenon may be of the same kind as, or at least analogous to, that observed by Faraday, viz., that when once an electric spark has passed through a gas the passage of another immediately afterwards is much facilitated, a fact confirmed by the experiments of Hittorf and Schuster [*].

The theory of Clausius in a more or less modified form has been almost universally adopted by chemists and physicists alike. Armstrong [†], however, practically rejects it on the somewhat slender grounds that it affords no explanation of the phenomena of electric conduction of certain silver salts in the solid state, and of the variations in conductivity of mixtures of sulphuric acid and water.

(ii.) *Period of Inertness followed by Acceleration.*

These phenomena were first noticed by Draper in the particular case of the reaction of hydrogen and chlorine gases under the influence of sunlight, and traced by him to an allotropic modification of the latter element [‡]. Similar observations were made by Bunsen and Roscoe in their investigations on the same subject, and the phenomenon was designated by them " Photochemical Induction " [§]; a term which has

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[*] *Cf.* also the recent experiments of J. J. Thomson on the electrolysis of steam (Proc. Roy. Soc. liii. pp. 90–110).
[†] Proc. Roy. Soc. xl. p. 271.   [‡] Phil. Mag. [3] xxvii. p. 328.
[§] Phil. Trans. 1857, p. 381.

been handed down through a series of manuals on Chemistry, the writers of which seem to consider that the phenomenon is necessarily conditioned by the agency of light. Bunsen and Roscoe make a mental presentation of resistance to be overcome before chemical change can commence. It is to be supposed, though the writers do not state it in so many words, that the term "induction" is based upon an analogy of magnetic and electric phenomena, called by the same term, which last just so long as the predetermining cause, namely the vicinity of an electrified or magnetized body.

The analogy is, however, incomplete in that though there are chemical changes which last as long as the external cause or condition, be it E.M.F., light, or heat, yet there are others which, when once commenced, will proceed, so far as can be judged, without the external agency. As the phenomenon is not necessarily dependent upon sunlight *, and as probably it is not entirely of a dynamical character, I have preferred to adopt the term " Inertness " or " Reluctance."

Bunsen and Roscoe further showed that when a mixture of hydrogen and chlorine gases, in which chemical change has set in under the influence of light, is darkened and then again exposed, the phenomena of inertness and initial acceleration are repeated; this observation, which has an important bearing on the course of chemical change, seems to have been quite overlooked by writers upon the subject. Pringsheim (*cf. supra*), repeating Bunsen and Roscoe's experiments, traces the above phenomena to the purely chemical cause of an intermediate reaction, basing the explanation on the fact that a mixture of hydrogen and chlorine gases was less susceptible to actinic rays when dry than when moist (an observation confirmed by Dixon†). Pringsheim considered the reactions to be as follows :—

$$\text{(i.)} \quad H_2 + Cl_2 + H_2O = Cl_2O + 2H_2,$$

$$\text{(ii.)} \quad Cl_2O + 2H_2 = 2HCl + H_2O,$$
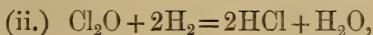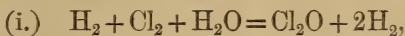
without, however, bringing forward any experimental evidence in support of the view, and, indeed, it is not probable that the anhydride Cl_2O would exist, as such, in the presence of water. But the investigations of Pedler ‡ supply the necessary data, in that he has shown that chlorine in the presence of

* Bunsen and Roscoe themselves also illustrate their results by others obtained in the study of the bromination of tartaric acid, a chemical change probably not wholly conditioned by actinic rays.
† Phil. Trans. (1893) [A], p. 144 (Bakerian Lecture).
‡ Journ. Chem. Soc. 1890, pp. 599–625.

water and under the influence of sunlight, the two conditions required, give hypochlorous acid as one of the initial products of the reaction ; the changes can therefore be written :—

$$\text{(i.)} \quad Cl_2 + 2H_2O = 2HClO + H_2.$$

$$\text{(ii.)} \quad 2HClO + 2H_2 = 2HCl + 2H_2O.$$
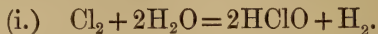
The above results afford a sufficient answer to the somewhat sceptical remark of Ostwald :—" Ueber die Natur der Zwischen-Substanz liess sich nicht bestimmtes ermitteln "*.

As regards this phase of the reactions of hydrogen with chlorine, Armstrong (Proc. Chem. Soc. 1893) writes :—" That no such irregularity is observed on heating iodine with hydrogen is not surprising, as hydrogen iodide would be formed from the very first, and the electrolyte present would exert a minimum resistance at once." But it is surprising that the reactions of hydrogen with chlorine and iodine respectively should ever be compared at all ; the only factors common to the two are the element hydrogen and the somewhat similar behaviour of the two resulting haloid acids. For the reaction between hydrogen and chlorine is conditioned, as everybody now admits, by the presence of water and by taking place at ordinary temperatures under the influence of sunlight, and under these conditions it is probably not reversible; further it is exothermic ($+22,000$ cals.), and some hydrochloric acid is formed after the lapse of about 2–4 minutes (Bunsen and Roscoe, Pringsheim). On the other hand, there is no experimental evidence at present to show that the reaction between hydrogen and iodine is conditioned by the presence of water ; it is unaffected by sunlight, as Lemoine † has shown that at ordinary temperatures and after one month's exposure to summer sun no appreciable combination takes place, though under the same conditions 80 per cent. of hydriodic acid is decomposed ; further, the reaction is reversible and endothermic (-800 cals.). Lastly, it is practically certain that hydriodic acid is not formed from the very first, as at a temperature of $200°$ $97·1$ per cent. of the hydrogen present in a mixture of iodine and hydrogen still remained free after an interval of $9\frac{1}{2}$ hours (Lemoine), which, to put it another way, would mean that only ·005 per cent. of the hydrogen has entered into combination after the lapse of one minute, presuming the change to proceed uniformly.

The phenomena of inertness and acceleration were also observed by Berthelot and Pean de Saint Gilles in their studies

* *Lehrbuch,* p. 1063.
† *Ann. Chim. Phys.* [5] xii. p. 207.

on the rate of formation of ethereal salts ; these writers gave [*],
without apparently being aware of the fact, the same ex-
planation as Bunsen and Roscoe.

Again, Hell and Urech (*cf. supra*) noticed these same
phenomena in their investigations on the bromination of the
acids of the acetic series ; they very cogently pointed out that
their results would be incomprehensible on the hypothesis
that the reaction consists in the simple substitution of hydrogen
by bromine, for in that case the maximum velocity should
be at the commencement of the reaction, when there is the
greatest mass of unaltered bromine present. These writers
seem to have been the first to give the probably true explana-
tion of this phase of chemical change, tracing it to the forma-
tion of an intermediate compound (in the particular case of
acetic acid to a body of composition $C_2H_4O_2Br_24HBr$) [†],
whereby a delay would of necessity be occasioned, and the
chemical change, though started, could only proceed at first
slowly.

It was noticed also by Harcourt in some unpublished in-
vestigations, and confirmed by later experiments of my own,
that the evolution of gases from homogeneous liquids as a
process of chemical change [‡] illustrates in a remarkable way
the same phenomena. These were especially observable in
the decomposition of potassium ferrocyanide with concen-
trated sulphuric acid, and in the reduction of nitric acid with
ferrous sulphate ; reactions in which intermediate substances
are undoubtedly formed, and, indeed, in the latter case the
progress of the change is rendered visible. In the course of
the experiments it was noticed that, if a liquid from which a
gas was being evolved was cooled and subsequently restored
to its former temperature, or if the superincumbent pressure
was suddenly increased from a third to one atmosphere, then,
though the evolution of gas was perfectly uniform before the
temporary alteration of condition, the phenomena of inert-
ness and acceleration were repeated in a greater or less degree.

Simultaneously Spring and van Aubel [§] noticed that the

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[*] *Ann. de Chim.* [3] lxvi. pp. 5–153. On the above point the authors
write as follows :—" Pour la concevoir il faut admettre une sorte d'inertie,
de résistance à vaincre qui retarde la combinaison ...; cette accélération
initiale semble donc constituer un caractère assez général de ce genre de
réactions."

[†] The writers do not bring forward much experimental evidence in
favour of the existence of this particular compound, but the formation of
unstable bromo-addition products, such as that of camphor for example,
is by no means infrequent among carbon compounds.

[‡] *Phil. Trans.* (1888) [A], p. 272.

[§] *Ann. Chim. Phys.* [6] xi. pp. 505–534.

velocity of the reaction between metallic zinc (containing ·6 per cent. of lead) and the halogen acid increases until it reaches a maximum ; these writers, however, apply again the term " induction." Precisely similar results were obtained by myself in the course of experiments on copper with diluted nitric acid *; if the conditions were such that the reaction commenced at all, then it started at first slowly. But these two latter examples will be more especially discussed in the sequel.

Again, it is a familiar fact to photographers that the action of light upon silver salts is less during the first period of exposure than subsequently ; the researches of H. B. Baker have shown that the chemical changes involved are extremely complicated by the formation of intermediate compounds.

The proposition set forth of the production of intermediate compounds can for simplicity be resolved into two general cases :—

(i.) In a chemical system compounds ab and cd unite to form a third compound $abcd$, which in its turn is resolved into compounds ac and bd thus

$$\text{(i.)} \quad ab + cd = abcd.$$
$$\text{(ii.)} \quad abcd = ac + bd.$$
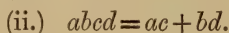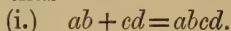
(ii.) A compound $abcd$ decomposes into compounds ab and cd, which subsequently react to form ac and bd, thus

$$\text{(i.)} \quad abcd = ab + cd.$$
$$\text{(ii.)} \quad ab + cd = ac + bd.$$
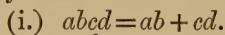
Both cases come under the category of concomitant variations, and the observations obtained in the course of experiments are not susceptible of mathematical analysis until the several amounts of reacting substances and products have been accurately ascertained. I have dwelt upon this phase of chemical change at some length, not indeed with the view of pointing out that changes proceed slowly at first, for this is patent to the merest tyro in experimental chemistry who pours some dilute sulphuric acid upon metallic zinc ; but rather I would wish to draw attention to the great importance of the study of intermediate compounds which are either generally overlooked or at best summarily dismissed as of no concern †. It is to my mind idle to discuss as to what may

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* Proc. Roy. Soc. xlvi. p. 217.

† The remark of Lord Rayleigh (B. A. Address 1884) is as pregnant as ever:—"If I might without presumption venture a word of recommendation, it would be in favour of a more minute study of the simpler chemical phenomena."

be or may not be, or whether certain "composite electrolytes" may or may not be formed ; for such discussions seem to reduce the fair field of experimental chemistry to the dry and arid waste of academical metaphysics.

(iii.) *Period of Constancy.*

This period has been observed in most of the cases discussed in the previous section, and would follow as a necessary consequence of two opposing factors, the one of acceleration, and the other of retardation due to the diminution of the masses of reacting substances. Its duration is therefore dependent upon the products of these factors ; and according to experimental conditions it has been observed to last either for the space of a few minutes or for several hours.

Berthelot's experiments have also shown that the velocity of propagation of explosive waves rapidly increases until a constant maximum is reached, the value of which varies with the nature of the exploding gases. Though the researches of Dixon [*] have conclusively proved that this maximum for the same pair of gases is dependent upon either the presence of moisture or of an excess of one of the gases, or of a third gas, whereby secondary reactions may ensue, yet, so far as I am aware, the effects produced on the earlier period of acceleration have not been made the subject of any elaborate series of experiments. I have therefore omitted their discussion in the preceding paragraph, though there can be but little doubt that in these cases also the formation of intermediate compounds (carbonic oxide, for example, as the first stage of the oxidation of carbon) would have a very important bearing.

(iv.) *Period of Diminishing Velocity.*

It is only necessary to allude to the final stage, so characteristic of all save reversible chemical changes, and which has so often been shown in the many elaborate memoirs published in the last thirty or forty years to be a function of mass, temperature, and other conditions.

WHAT IS CHEMICAL CHANGE?

In the preceding paragraphs the course of chemical change has been discussed ; we now pass on to the more difficult problem concerning its nature.

Some sixty years ago Faraday, impressed, doubtless, with his wonderful experiments upon electrolysis, wrote [†] :—" The

[*] Phil Trans. 1884, p. 617, and 1893 [A], pp. 97–188.
[†] 'Experimental Researches.'

forces termed chemical affinity and electricity are one and the same," a sentence which has become the text of the discourses of numerous writers in the present generation. With somewhat more reserve Helmholtz [*] put forward the view that " the very mightiest among chemical forces are of electric origin," which is another frequently quoted text.

Of course everybody will grant that the chemical changes in a battery and electrolytic cells are identical both in kind and quantity ; everybody also will allow that chemical change and E.M.F. are frequently interdependent variables, and lastly the ionic dissociation theory has a whole school of followers. But it is not as yet possible (notwithstanding a certain array of experimental evidence) in our present state of knowledge to accept Armstrong's definition of chemical change as " reversed electrolysis " [†], or the proposition, not wholly identical with it, that in order that chemical change may take place the system operated upon should comprise an electrolyte. For, on the one hand, there are cases of chemical change which do not occur even in the presence of an electrolyte, and, on the other, there are cases which occur even in the absence of an electrolyte.

For example, it will not be denied that dilute hydrochloric, sulphuric, and nitric acids are electrolytes *par excellence* ; yet for all that certain metals in a state of purity will not dissolve in them. But if, before introduction of the metal, an electric current be passed through these several acids, whereby (possibly) persulphuric, nitrous, and oxygenated chlorine acids are produced, then under these circumstances chemical reaction ensues. Thus electrolysis causes the formation of some intermediate compound ; is it logical, therefore, to conclude that electrolysis is the necessary antecedent and concomitant of its own reverse ?

Again, to take an example from everyday life, the materials of a common match-head and box do not apparently contain an electrolyte, yet the chemical change is violent enough when one is rubbed against the other. At present we are without evidence to show that no change would take place if this everyday experiment were performed with absolutely dry materials (especially the potassium chlorate) and in an absolutely dry atmosphere.

It seems most rational to suppose that mechanical is converted into heat-energy, which is subsequently degraded by the combustion of the substances present.

[*] Journ. Chem. Soc. 1881, p. 277.

[†] Proc. Chem. Soc. 1885, p. 40; also British Association Report, 1885, p. 953.

Again, the electric conductivity of hydrocarbons is for the most part extremely small, yet in many cases they readily enter into chemical change at ordinary temperature without the intervention of extraneous energy. For example, many of them combine directly with bromine with extreme violence, yet it could hardly be supposed that a trace of hydrobromic acid formed as a by-product in the midst of an insulator is the determining cause. The reactions of the zinc and other organo-metallic compounds upon oxygenated compounds presumably dry are also examples of changes wherein there is as yet no evidence to show that they are dependent upon the presence of an electrolyte, or that they are of the nature of reversed electrolysis. Such examples might be multiplied, and will readily occur to any student of chemistry.

Lastly, is there any evidence to show that chemical changes induced by finely divided platinum are conditioned by the presence of an electrolyte? or any proof that moisture, or some other " tertium quid?" must be present? or generally, has any satisfactory explanation of the nature of surfaces been given? " Catalytic reactions are reactions which we do not understand," this has become a by-word and a reproach among chemists. Guesswork as to what may be is of no avail ; we want to know what is. In any case there seems nothing to warrant the exclusive selection of two particular forms of energy, namely the electric current and chemical affinity, and to define absolutely the latter as the reverse of the former. For with equal reason, and with as fair a show of argument, heat and chemical energy might likewise be defined as terms mutually reversible. Probably the true position of the case is most exactly summed up by the quotation from Helmholtz's writings given above, that some of the very mightiest among chemical forces are of electric origin.

What is the cause of the commencement of Chemical Change?

Of recent years the reactivity of substances has been considered to be conditioned by the degree of ionic dissociation, the measure of which is expressed by the factor

$$x = \frac{u_1}{u_\infty},$$

wherein u and u_∞ are the molecular conductivities at any particular and at infinite dilution. This hypothesis has been so widely accepted, not only as affording a convenient

explanation of the commencement of chemical change but also as being supported by evidence derived from a study of other physical phenomena *, that it would seem to savour almost of ultra-conservatism † to pass any criticism upon it.

On all sides it is admitted that if the hypothesis of ionic dissociation be granted other phenomena would follow as logical consequences ; and of these no other explanation has been given, though they are not wholly otherwise unintelligible. But the propounders of this theory seem at best to slur over the initial difficulties, and to postulate properties of certain kinds of matter of which, *ex hypothesi*, we can have no cognition.

To take the more commonly selected example : it is supposed that when potassium chloride is dissolved in excess of water it is more or less dissociated into free potassium and free chlorine atoms, each with enormous electric charges, equal and opposite in kind. It is further assumed ‡ that the free potassium ions are a kind of matter different from a lump of potassium, and that the free chlorine ions are a kind of matter different from chlorine gas in a jar, somewhat as yellow and red phosphorus are different kinds of matter. Writers allow that there is no exact knowledge of the amount of these electric charges, and, indeed, if according to the hypothesis these are equal and opposite in kind, there seems to be some difficulty in devising any experimental method for their measurement. But they consider that it is a matter of acquired knowledge that the chemical and physical properties of elementary substances are greatly altered and almost nullified by electric charges imparted to them by the mere process of solution of their compounds in water. A lump of potassium is regarded by this school of writers as made up " of mole-

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* For a review of the position *cf.* Arrhenius, " Chemical Theory of Electrolytes," Acad. Science, Sweden ; also W. N. Shaw, B. A. Report, 1891, who gives the references to the literature upon the subject.

† One can hardly refrain from quoting the following passage from Nernst's work *Theoretische Chemie* (Stuttgart, 1893), as an example of self-satisfactory dogmatism almost unequalled in any scientific publication :—" Es ist hier natürlich nicht der Ort, auf den Inhalt einer derartigen unfruchtbaren Opposition, die auch nicht ein einziges neues Moment zu Tage förderte, und die daher am besten einer schnellen Vergessenheit anheimfiele, näher einzugehen."

‡ Writers upon this subject seem almost to consider that no assumption is here implied ; thus Ostwald (*Lehrbuch der allgemeinen Chemie,* Leipzig, 1893, p. 784) writes :—" Die Aufklärung des scheinbaren Widerspruches liegt so viel darin, dass ' freies Kaliummetall ' und ' freie Kaliumionen' ganz verschiedene Dinge sind ; sie sind nicht identisch, sondern nur isomer." This last sentence would imply a definite statement of fact.

cules * consisting of an unknown and probably great number
of potassium atoms," even though the determination of its
molecular weight, alike by the methods of vaporization, the
depression of freezing-points, and diminution of vapour-
pressure, would point to a molecular number 39·1, if that of
hydrogen be taken as 2. Thus the only point of differentiation
is the assumed enormous electric charge. But even if it be
granted that such a charge would alter the properties of
a kind of matter (of which, be it remarked, there is no expe-
rimental evidence) precisely as yellow phosphorus is converted
by the process of heating into red phosphorus, yet the dif-
ference between these two last modifications is for the most
part one of degree and not one of kind. But we are asked to
believe that ionic potassium would not decompose water, and
that ionic chlorine would possess no odour.

The propounders of this hypothesis take away attributes
hitherto regarded as essential to the various elementary kinds
of matter, and substitute for them mere mental abstractions.
As such they might be useful in the same sense as circles and
triangles, and we might possibly deal with them as implied
postulates ; but to predicate properties of kinds of matter of
which we can have no cognition, and to differentiate them
from kinds of matter of which we have cognition, is to carry
scientific imagination beyond its legitimate bounds. The
following sentences taken from Ostwald's *Lehrbuch* illustrate
the relations given in the text :—(i) " Chlor is ein stark
riechendes Gas ; " (ii) " Das molekulare Chlor, Cl_2, geht in
Chlorionen über ; " (iii) " Ebenso muss in Gefässe B ein
Ueberschuss von Chlorionen vorhanden sein . . . in keinem
Gefässe nimmt man etwas besonderes wahr—weder . . . noch
Chlorgeruch in B."

Though the element chlorine when combined with potassium
in potassium chloride or with hydrogen and carbon (in
chloroform, for example) has none of the properties of ele-
mentary chlorine by itself, yet this would not affect the
question ; for by the ionic dissociation theory the chlorine in

* It is time to protest against such a sentence as this in a book (Nernst,
cf. supra) written presumably, as our English phrase hath it, " for the use
of schools and colleges " :—" Wasserstoff und Chlor sind uns beide bei
gewöhnlicher Temperatur nur als H_2 und Cl_2 *bekannt.*" We know the
properties of hydrogen—or at least we have a rational expectation,
amounting almost to a certainty, that the properties of a specimen
of hydrogen collected to-day are the same as those of a specimen of
hydrogen collected fifty years ago; but we do not *know* hydrogen as H_2.
All that we can say is this, that, adopting certain hypotheses of the con-
stitution of matter, we believe, or we imagine, or at best we conventionally
represent the molecule of hydrogen to be H_2.

dissolved potassium chloride is considered to be free, or at least not combined with the potassium. Williamson pointed out years ago that it is not strictly accurate to speak either of the element potassium or the element chlorine as present in potassium chloride, and, indeed, there is a certain inconsistency in modern nomenclature in that one element and not the other is put in the adjectival form.

It can be argued that an asymmetric carbon atom is likewise a mental abstraction; but specific attributes are not predicated of such a carbon atom—all that is or can be done is to put forward this abstraction as a working hypothesis to explain the constitution of certain carbon compounds. Molecules also are ideals, but we cannot predicate of them any attributes, whether of sphericity or non-sphericity, of elasticity or inelasticity : as we may apply the ideal geometrical triangle for the more real triangle of velocities, so likewise we apply our ideal molecules to solve problems on the velocities of congeries of them.

But certain writers incline to draw students away from the main issue by a distinction between heat-dissociation and ionic or electrolytic dissociation (both terms being unfortunate enough). Thus to select a case, these statements are made equally as of matters of fact [*]:—" If sal ammoniac is dissolved in a large quantity of water it is electrolytically decomposed almost completely in accordance with the equation

$$NH_4Cl = N\overset{+}{H}_4 + \overset{-}{Cl},$$

and if we vaporize it under sufficiently low pressure, it decomposes again in accordance with the equation

$$NH_4Cl = NH_3 + HCl,$$

viz. in unelectrified molecules. *Both are quite different phenomena, the interdependence between which, even if probable, is not yet known.*"

The former reaction is, however, quite theoretical, and we have no manner of means of identifying the presence of the hypothetical radical, NH_4, or the electro-negatively charged elementary substance chlorine, possessing hypothetical pro-

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[*] The original is here appended :—" Löst man Salmiak in viel Wasser auf, so dissociirt er sich fast völlig in Sinne der Gleichung . . . electrolytisch, und vergasen wir ihn unter hinreichend kleinem Druck, so zerfällt er wiederum sehr weit gehend in Sinne der Gleichung . . . in unelectrische Molecule. *Beide sind ganz verschiedene Vorgänge, zwischen denen ein Zusammenhang, wenn er auch wahrscheinlich, so doch nicht erkannt ist.*" Nernst, *cf. supra.*

perties; whereas we can identify, by suitable mechanical means, in vaporized sal ammoniac the real gases ammonia and hydrochloric acid. Yet, forsooth, there may be a relation between these two phenomena, and we teach boys in our public schools that chemistry is an exact science! But apart from these arguments, which are based upon the nature of the evidence of the phenomena in themselves, without considering others which may or may not be logically deduced from them, there is further the dilemma, pointed out alike by Armstrong * and Pickering †, that those compounds which we regard as most undecomposable are precisely those which electrolytically most decompose, and this, too, as an effect of solution in water, generally considered a relatively inert material.

Here, again, Prof. Ostwald would seek to draw us into a side-issue by the supposition that his opponents would confound *stability* with *reactivity*. The *stability* of a compound is generally represented as an attribute of it with reference to the decompositions produced by forces other than chemical; its *reactivity* is an attribute of it with reference to those forces which we call chemical. Yet the *reactivity* of substances is considered to be a function of their electrolytic dissociation, or their instability when dissolved in water.

Again, the argument brought forward by Pickering ‡ seems as yet to have been unanswered and to be well-nigh unanswerable, namely, that if we acknowledge the doctrine of electrolytic dissociation we must deny the principle of the conservation of energy, for which there is an abundance of direct evidence. This writer has pointed out, as one example out of many, that if two molecular proportions of hydrochloric acid, when dissolved in water, be entirely dissociated into their individual atoms, there must be an absorption of $44,000 + x + y$ cals., whereas, as a matter of fact, there is an evolution of $34,630$ cals., or a creation of an amount of energy represented by $(78,630 + x + y)$ cals. out of nothing and from nowhere.

In fact many writers of the present day seem to deal with electric and chemical forces or electrified and non-electrified atoms as two cards in a kind of game of blind-hookey, either of which may be turned up at will.

But there is the real dilemma of the reactivity of substances

* 'Electrician,' August 26th, 1887.
† Phil. Mag. [5] xxix. p. 425.
‡ *Cf. supra.*

when moist *, as compared with their inertness when dry. The non-combustibility of charcoal, sulphur, and phosphorus in oxygen, the non-combination of ammonia with hydrogen chloride, the inappreciable change when undiluted acids are poured upon carbonates, and a host of other examples might be cited. Upon this point Ostwald, on the one hand, appears to beg the whole question when he writes that, "as probably there is no absolute non-conductor, there is the possibility in all cases of assuming the existence of at least a few ions." On the other hand, Armstrong would assign to "water special properties which enable it to act directly; moreover—perhaps because—in such cases composite electrolytes would result." On both sides, be it noted, we are asked to be content with mere possibilities, which are even more unsatisfactory in the science of chemistry than they are in matters of real life.

As yet there seems to be no answer forthcoming to the question, Why does chemical change ever begin?

The Reaction of Acids with Metals.

The particular case of these reactions I have proposed to consider separately, partly on account of its practical importance, partly also to deal with another "eidolon" of chemistry, nascent hydrogen, and lastly because I have been more specially interested with the problem. In former years, and possibly even to this day, it was customary to teach that both zinc and copper, for example, directly displace hydrogen from sulphuric acid; but in the first case the gas is liberated as such, while in the latter it is nascent and reduces the sulphuric acid to sulphur dioxide. So also the more complicated results of the reaction of metals with nitric acid have been supposed to be the successive products of the reduction of the acid by nascent hydrogen of greater or less activity.

As to the latter problem, and more especially with regard to the metals silver, copper, mercury, and bismuth, it was originally shown by Millon † for the first three metals, subsequently more completely by Russell ‡ for silver, and finally by

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* Apart from the Baconian maxim, "Corpora non agunt nisi soluta," the following passage shows that the necessity of water for chemical change had been the subject of observation even at the commencement of the present century :—" Pure calcareous earth (lime) will have no effect on muriatic gas when both are perfectly dry; yet water, to which the gas has no chemical affinity, will condense it : in this state it will readily form an intimate union with the lime" (Higgins, 'Experiments and Observations on the Atomic Theory,' 1814).

† *Comptes Rendus,* xiv. pp. 904–912.

‡ Journ. Chem. Soc. 1874, pp. 3–12.

myself* for the last three, that these several metals do not dissolve in nitric acid, but if the reduction-product of nitr acid, be it nitrous acid or nitrogen peroxide, is present, then these metals dissolve. To put the facts in a logical form :—
(i.) These metals do not dissolve in nitric acid ; (ii.) these metals do dissolve in nitric acid containing nitrous acid †. Unfortunately at present there seems to be no means of proving the third term, namely, that these metals do not dissolve in nitrous acid, though it is clearly demonstrated that the amount of metal dissolved varies not with the amount of nitric acid within certain limits, but with the amount of nitrous acid. It must therefore be concluded that the presence of the nitrous acid is the cause, or a necessary part of the cause, of the phenomenon of the solution; and it would follow that, whatever be the correct interpretation of the chemical change, nitric acid is not the actual solvent of the metal. Indeed my own experiments have shown that, within limits, the presence of an excess of nitric acid not only does not increase, but actually retards the solution of the three metals copper, mercury, and bismuth. But Armstrong conceives that " the hydrogen of the acid is virtually directly displaced by the metal with the assistance, however, of the current-energy derived from its own oxidation by the nitrous compound " ‡. There are, therefore, at least two interpretations of the problem : First, it is supposed that the hydrogen of the acid is displaced, and this in the nascent condition, or somehow or another, reduces the nitric to nitrous acid, thus:—

$$2HNO_3 + M = M(NO_3)_2 + H_2,$$
$$HNO_3 + H_2 = HNO_2 + H_2O ;$$

or $$2HNO_3 + H_2 = N_2O_4 + 2H_2O.$$
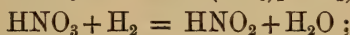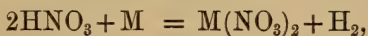
Secondly, it may be supposed that the nitrous acid or nitrogen peroxide is formed from the nitric acid *per se*, and then the metal can be dissolved thus :—

(i.) $$HNO_3 = HNO_2 + O,$$
(ii.) $$2HNO_2 + M = M(NO_2)_2 + 2H_2O + 2NO ;$$

or
(i.) $$2HNO_3 = N_2O_4 + H_2O + O,$$
(ii.) $$M + N_2O_4 = M(NO_2)_2.$$
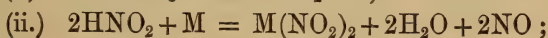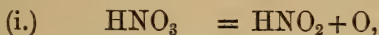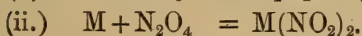
* Phil. Trans. 1891 [A], pp. 279–317.
† I use the term " nitrous acid " rather for the sake of brevity, and without wishing to exclude the possibility that the active material is really nitrogen peroxide.
‡ Armstrong, Proc. Chem. Soc. 1892 ("On the Nature of Depolarisers")

The first view is based upon the analogy of the solution of certain metals in sulphuric acid, whereby hydrogen is set free, and also upon the argument that this same gas is set free, when metallic magnesium is dissolved in nitric acid; but it appears that, if we accept this view, a certain property, namely that of reducing nitric acid, is attributed to the element hydrogen when in a certain condition (to which also is superadded a current-energy), which it does not possess in the state or condition in which we know it. The general conception is that the element hydrogen in the former case is " atomic " and in the latter is " molecular," though it is to be observed that the relations of atoms to molecules are in obscurity. That is to say, four distinct hypotheses are involved:—(i.) that of nascent hydrogen; (ii.) that nascent hydrogen is atomic; (iii.) that nascent or atomic hydrogen differs in its attributes from hydrogen as we know it; and (iv.) that hydrogen, as we know it, is molecular. Further, it does not seem safe to argue from the reaction of magnesium with nitric acid to those of copper &c. with the same acid, for at present there is no evidence to show that the solution of magnesium in the acid is dependent upon the presence of nitrous acid. If this is shown not to be the case, *cadit quæstio*.

The often-cited argument in favour of the nascent hydrogen hypothesis, namely, that no reduction ensues when hydrogen gas is passed through nitric acid, appears to be rather beside the question, for on the one hand the contact between a gas and a liquid is very incomplete, only the outer shell of each bubble being affected, and on the other the stream of the gas would mechanically blow off any nitrous acid (or nitrogen peroxide) which might be formed.

The argument from the reactions supposed to take place in the Grove's cell seems also to be beside the point, since there must be a certain amount of interdiffusion between the nitric and sulphuric acids which would complicate the chemical changes. But, on the other hand, the following facts support the view that the nitrous acid or nitrogen peroxide is formed initially from the nitric acid *per se* :—First, the more concentrated acid very rapidly turns yellow from the formation of nitrogen peroxide, when exposed to the sunlight, but more slowly when the acid is kept in the dark or diluted. Further, my experience has shown that even the jolting of a railway journey is sufficient to increase the proportion of the nitrous compound even in the case of acids of about 30 per cent. concentration. Secondly, the same change is very readily effected by the presence of organic matter, which it is well-nigh impossible to eliminate from the air of laboratories.

In the course of the investigations conducted by Burch and myself on the E.M.F. of certain cells containing nitric acid, it was continually found that if the containing vesssel was not clean, if the metallic strips were touched with the fingers, or if the strips were not thoroughly cleansed, the E.M.F. of the cell rose to its maximum at once. It is quite clear, therefore, that a trace of the nitrous compound could be formed in numerous ways, and, when once formed, would tend to increase in the presence of the metal. The recent investigations of Sabatier and Sanderens * have shown that finely divided copper readily absorbs nitrogen peroxide at ordinary temperatures to produce a nitro-copper of composition Cu_2NO_2, upon which water reacts with violence to give a solution of copper nitrate and nitrite, nitric-oxide gas being evolved.

Though it is not wholly safe to argue from the results of experiments conducted under one set of conditions to those conducted under another, yet it is remarkable that the products of the reaction of copper with diluted nitric acid are in the main identical with those of water with the nitro-copper. The conclusion is not, therefore, wholly improbable that the nitrogen peroxide present in the nitric acid combines with the copper to form intermediately the nitro-copper, which in its turn is decomposed by the water to re-form the nitrous compound. The researches of Freer and Higley † have further shown that in the case of concentrated acids the main product of the reaction of metallic copper is nitrogen peroxide.

It is also remarkable that metallic lead dissolves very rapidly in the liquid obtained by the addition of nitrogen peroxide to water ‡, even though of a less degree of acidity than other mixtures of nitric acid and the nitrous compound, though here again it is not wholly safe to argue from the results obtained in the case of one metal to those of another. At present I am engaged upon this point for metals other than lead. If, then, the formation of nitrogen peroxide be accomplished, then not only will nitric oxide result, but also the more deoxidized products such as nitrous oxide and nitrogen will be produced from subsidiary reactions between the nitric acid and the metallic nitrates. The formation, therefore, of all the products in the case of the metals mercury, copper, silver, and bismuth can readily be explained without recourse to the convenient hypothesis, nascent hydrogen. But at present there is no satisfactory explanation of the formation of ammonia and hydroxylamine, and this mainly for the

* *Bull. Soc. Chim.* [3] ix. pp. 669–674.
† Amer. Chem. Journ. 1893, p. 71.
‡ Journ. Soc. Chem. Indust. 1891.

reason that the reactions between nitric oxide and metallic nitrates have hitherto received but little attention.

The reactions of metals with sulphuric acid have not been the subject of many investigations, partly, no doubt, from their assumed simplicity. Even at present there is no exact knowledge as to the nature of the intermediate substance formed from the sulphuric acid, which enables the metal to dissolve and to continue dissolving ; probably it is some product of electrolysis, for it has been shown that pure zinc dissolves in diluted sulphuric acid through which an electric current has been passed, though no reaction ensued between the same samples of zinc and sulphuric acid previous to the passage of the current. Yet, whatever this substance may be, if the metal dissolves in the dilute acid, there are always formed traces, however small, of products other than hydrogen, and especially of hydrogen sulphide, while cadmium (which in many other respects resembles zinc) gives such reduction-products that the liquid turns milky with formation of sulphur.

The reaction of copper and allied metals with concentrated sulphuric acid is generally represented as taking place in two successive stages, namely, first the direct replacement of the hydrogen by the metal, and, secondly, the reduction of the sulphuric acid by the nascent hydrogen, thus :—

$$(1) \quad Cu + H_2SO_4 = CuSO_4 + H_2 \; ;$$
$$(2) \quad H_2SO_4 + H_2 = 2H_2O + SO_2.$$
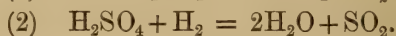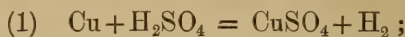
But here, again, there seems to be but little necessity for the hypothesis of nascent hydrogen, for the reaction only ensues with more concentrated acid, in which there is a greater tendency towards a decomposition of the acid into the trioxide and water, and the metallic copper may reduce the former with formation of cupric oxide and sulphur dioxide. Or, if the solution of the metal, as that of zinc in sulphuric acid, is dependent upon some product of electrolysis, the metal *per se* may directly reduce this. Though neither of these views is as yet confirmed by experimental investigation, yet both appear to be more probable than that of nascent hydrogen.

Investigations upon the conditions of formation and function of these intermediate compounds are greatly wanted, especially as the chemical changes between metals and acids resemble others discussed above, in that they pass through the same successive phases.

The University Museum, Oxford.

XIV. *A Study of the Polarization upon a Thin Metal Partition in a Voltameter.*—Part I.   *By* JOHN DANIEL*.

[Plates III. & IV.]

Introduction.

THE curious polarization phenomena of very small electrodes in a sulphuric-acid voltameter bearing a strong current, accounts of which appeared in the *Annalen* during the winter of 1892, suggested to Dr. L. Arons, of the University of Berlin, to try a very thin metal partition in a voltameter, expecting, as he said, that there would be a development of heat at this partition, resulting in the destruction of the partition.   Dr. Arons used gold-leaf as a partition. The gold-leaf was pasted with canada balsam over a hole about 15 millim. in diameter bored in a glass plate, which was slipped into the groove of a wooden or vulcanite frame in the middle of the voltameter.   This did not give a tight partition, but sufficed for the observation that there was not even visible development of gas on the gold-leaf; whereas platinum ·02 millim. thick, substituted for the gold-leaf, showed profuse development of gas with the current-strength used, even when punctured with a hole 2 millim. square.   I think Dr. Arons also tried the gold-leaf partition in a solution of Cu or Ag salt, and observed that the metal was deposited on the partition.

At the suggestion and under the kind direction of Professor A. Kundt and Dr. L. Arons I undertook a more thorough investigation of the subject.   Several problems presented themselves :—

(1) By quantitative measurement to determine whether there be a critical thickness below which there will be no polarization at the partition, and, if so, to determine this thickness.

(2) To determine the other critical thickness for which the polarization is as great as for very thick plates.

(3) The quantitative measurement of this polarization with the same current-strength for plates of various thicknesses between these limits.

(4) By varying the current-strength in these different cases, to determine what function the polarization is of the current-strength.

(5) To learn how the polarization in these cases varies with the time during which a given current-strength flows, readings

* Communicated by Prof. O. J. Lodge, D.Sc., F.R.S.

being made periodically until the polarization becomes constant, or nearly so.

These are the principal direct problems that have been attacked. Numerous minor observations have been made and will be discussed in their place. The experiments have been made in a room of fairly constant temperature, and no attempt has been made to account for slight variations of temperature as affecting resistance &c., as the quantities to be measured are interesting mainly as regards their relative values; but especially because such a slight correction would be cloaked by such unavoidable variations as irregular escape of gas from the electrodes or partition, in case of its development there.

Apparatus.

The instruments employed as well as the plan of the experiments are very simple. As a galvanoscope as well as current-measurer, a well-damped ring-galvanometer was used. The galvanometer had four coils of about 22 ohms each, which could be connected as desired. Deflexions were read with a telescope on a scale divided into millimetres, fixed at a distance of 1·5 metre. The instruments were supported by an independent stone pier. As nearly as possible the same deflexion of the galvanometer was always used, the resistance being so adjusted as to effect this; and the "figure of merit" of the galvanometer for this position was determined by connecting a Daniell cell with the galvanometer in series with a known resistance of such value as to give the deflexion to be used, and found to be, by Ohm's law,

$$\gamma = 0 \cdot 000000265 \text{ ampere per scale-division.}$$

For a new position used later, $\gamma = \cdot 000000224$.

The connexions for the galvanometer circuit are shown in fig. 1.

(a) To measure the strength of current flowing through the voltameter at any time, we observe the scale-deflexion, and apply the following simple relations of current and resistance, by Kirchhoff's law :—

(1) $I = i_1 + i_2$.

(2) $i_1 r_1 = i_2 r_2$, but $i_2 = \gamma a$, and $r_2 = 1100$, always;
      $\therefore$ $1100 \times 0 \cdot 000000265 \times a = i_1 r_1 = i_2 r_2$.

Here, r_1 being known, i_1 is determined, and from (1) I is found. The shunt resistance, r_1, was changed as the main resistance, R, was altered so as to maintain the same deflexion of the galvanometer.

(b) For measuring the ohmic resistance of the voltameter, Kohlrausch's method with induction-coil and electrodynamometer was used. The connexions for this measurement

Fig. 1.
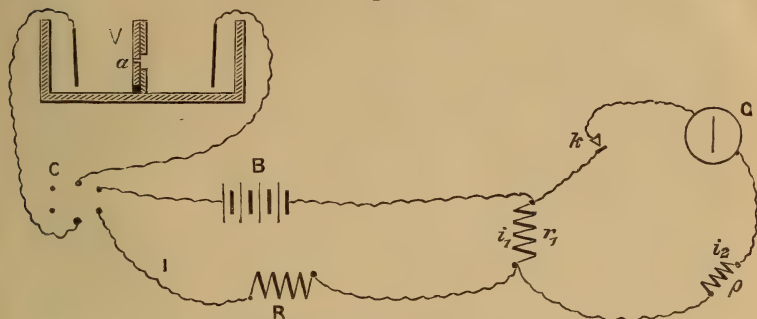
B = battery of storage-cells.
V = voltameter, with partition, a.
C = commutator.
G = galvanometer, with key, k, to close circuit.
R = auxiliary resistance in the main circuit.
r_1 = resistance to which the galvanometer circuit is shunt.
ρ = auxiliary resistance in galvanometer circuit, = 1010 ohms.
r_2 = total   ,,   ,,   ,,   ,,   = 1100   ,,
I = main current in amperes.
i_1 and i_2 = currents in the respective branches.
v = ohmic resistance of the voltameter.
r_3 = resistance of connexions.

Fig. 2.
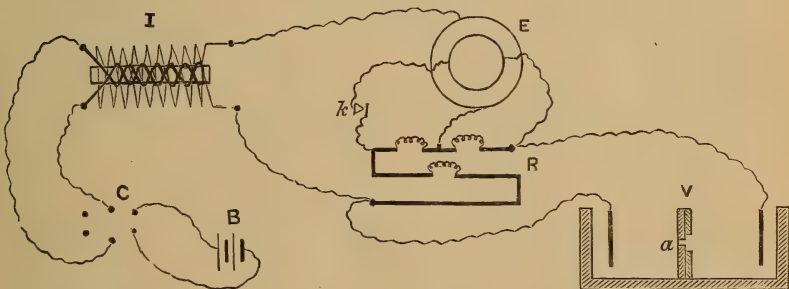
B = battery.
C = commutator.
I = induction-coil.
E = electrodynamometer, with key, k, in movable coil-circuit.
R = P.O. box.
V = voltameter.

are indicated in fig. 2. A solid iron core was used in the induction-coil to avoid the great difference in the direct and inverse currents which exists when a wire core is used, and which results in a polarization of the voltameter. The P.O. box was used as a Wheatstone bridge, of which the voltameter was one arm, and the movable coil of the electrodynamometer was connected across the branches of the bridge in the usual "null method" fashion, the fixed coils being in series with the main circuit. Being thus used only as a galvanoscope, its constant need not be discussed; suffice it to say that the arrangement was sensitive to several decimals, though resistance was measured only to hundredths of an ohm.

(c) The voltameter is simple, though its construction involves the only novelty in the apparatus. The voltameter first used was a glass vessel, 18 centim. long, 6 centim. wide, 8 centim. deep, with a hard rubber partition, sealed-in with sealing-wax, in the middle. The opening in the vulcanite was 3 centim. wide, and extended to within 2 centim. of the bottom. This frame for the partition was made by sealing two pieces of vulcanite together with a rim of the same between, of the same thickness as the glass plates bearing the metal partitions, which were slipped down into the groove thus formed. This was convenient, as the plates could be easily and quickly changed; but a quantitative test showed leakage around the edge of the glass plate of nearly 20 per cent. of the conductivity when the plate was open, using solid and bored glass respectively: hence the results obtained with this voltameter are only relative, not quantitatively correct. This voltameter and its results would not be mentioned here but for the fact that I was so careless as to think that this tight-fitting glass would not allow sensible leakage under the circumstances, and so made a long series of measurements before testing the leakage quantitatively, and, too, with some solutions which I have not had time to repeat with the

Voltameter as finally adopted.

This consists of a glass vessel 20 centim. long, 12 centim. wide, 11 centim. deep. In the middle is fixed by sealing-wax a plate-glass partition 3 millim. thick, with a hole in the centre 2 centim. in diameter. A smaller glass plate, with hole 1·5 centim. in diameter, is sealed over this opening, the metal partition being first sealed over the hole in the small glass. This gives two water-tight compartments, which also offer no electrical communication except through the metal under

experiment, which covers the hole in the glass. The end electrodes are of platinized platinum, 4 by 6 centim. and 0·1 millim. thick. With $CuSO_4$ solution, Cu electrodes were used. Very thin plates of metal, even ordinary gold-leaf, were easily sealed over the hole in the small glass plate by laying the foil on smooth paper, carefully melting sealing-wax placed around the hole in the form of powder, and then cautiously picking the thin metal up with the melted wax. This being safely accomplished, sealing the small glass plate over the opening in the partition is easy. Each side of the voltameter could then be filled up to the lower edge of the opening at once : then, by carefully pouring the solution alternately in the two sides a little at a time, using a glass rod, the vessel was filled above the gold-leaf, which showed surprising strength in being able to stand a difference of level of several millimetres.

For the voltameter in fig. 1 we have the following relations :—

(A) The voltameter included in the circuit and the partition open,

$$I = \frac{E - e}{R + r_3 + \dfrac{1}{\dfrac{1}{r_1} + \dfrac{1}{r_2}} + v}.$$

We are concerned only with the *change* in the auxiliary resistance, and not its absolute value, in order to make the current the same when the partition is changed, and hence may simplify the case by representing the sum in the denominator by W. Therefore

(1) $I = \dfrac{E - e}{W}$, with partition open,

(2) $I = \dfrac{E - e - x}{W - w}$, with metal partition,

$\therefore \dfrac{E - e}{W} = \dfrac{E - e - x}{W - w},$

$\therefore x = w \left(\dfrac{E - e}{W} \right) = I w.$

    (A) $x = I w =$ polarization on partition.

(3) $I = \dfrac{E}{W + w_1 - v}$, with voltameter cut out of the circuit.

$\therefore$ from (1) and (3),

    (B) $e = I (w_1 - v) =$ polarization on end electrodes.

In every case the auxiliary resistance was so adjusted as to

make the current as nearly as possible the same with partition in and partition out. This could not be done exactly, but was corrected by interpolation. We shall be mainly concerned with the polarization on the partition ; and we see from (A) that this polarization, expressed in volts, is the simple product of current-strength in amperes, and the *change* of resistance necessary to keep the current the same when the partition is added that it was with partition open.

The same box of resistance was used for all purposes—in determining the "figure of merit" of the galvanometer, the resistance of the voltameter, and as rheostat to regulate the main and branch currents ; hence we are not concerned with the question as to whether the units are true ohms, as it does not affect our results.

Solutions used as Electrolytes.

With the old voltameter relative values have been obtained for 30 per cent. H_2SO_4, 5 per cent. H_2SO_4, and very dilute H_2SO_4, such as to give voltameter resistances of 20, 60, and 100 ohms, about. With the new voltameter, quantitative measurements have been made with

30 per cent. H_2SO_4 ; sp. gr. $= 1\cdot22$; $v = 1\cdot1$ ohms.
„   „ $CuSO_4$;   „ $= 1\cdot12$; $v = 24\cdot5$ „
„   „   NaCl ;   „ $= 1\cdot12$; $v = 5\cdot5$ „

Also some observations with

3 per cent. H_2SO_4 ; sp. gr. $= 1\cdot2$;
„   „   KOH ;   „ $= 1\cdot11$;

and *very dilute* sulphuric acid.

As partitions in the voltameter, platinum, gold, silver, and aluminium have been used, such as are described below. The thickness of the thick plates was measured with a micrometer-gauge ; that of the thin plates was calculated from their size, weight, and specific gravity. The plates marked S. & W. were from Sy and Wagner, of Berlin, and are supposed to be quite pure. Those marked M. are from Müller, of Dresden, and are, some pure, as indicated, others of the quality of the finest gold-leaf, *i. e.* $0\cdot925$ pure. It will be convenient in the Tables to refer to these partitions by the *numbers*, and the following description will suffice once for all.

Thickness of Partitions.

Platinum.	Gold.
millim.	millim.
#1; S. & W. ; pure; $=0\cdot1$.	#0; S. & W. ; pure; $=0\cdot25$.
#2; „ ; „ ; $=0\cdot002$.	
#3; M. ; „ ; $=0\cdot000152$.	#1; M. ; „ ; $=0\cdot0472$.
#4; S. & W. ; „ ; $=0\cdot0173$.	#2; „ ; $\frac{925}{1000}$; $=0\cdot0241$.
#5; „ ; „ ; $=0\cdot00407$.	#3; „ ; „ ; $=0\cdot00433$.
Silver.	#4; „ ; „ ; $=0\cdot00183$.
#1; S. & W. ; pure; $=0\cdot0023$.	#5; „ ; „ ; $=0\cdot000586$.
Aluminium.	#6; „ ; „ ; $=0\cdot000382$.
#1; commercial; $=0\cdot4$.	#7; „ ; „ ; $=0\cdot000087$.
#2; „ ; $=0\cdot00051$.	

The series of gold plates is fairly complete. They were beaten to order by Ferdinand Müller in Dresden. Effort was made to get a similar series of platinum; but as platinum-foil for " silvering " seems to have fallen into disuse, I was unable to find anyone prepared to make it for me. This is unfortunate, as platinum is the only metal which seems to remain free from chemical action under a strong and long-continued electric current. However, as #2 and #3 of the platinum happen to fall below and between the critical limits respectively, they serve as a very important check upon the results obtained with the more complete gold series, and show that these results are at least qualitatively correct. Below will be found reasons for believing them to be quantitatively correct.

In the Tables which follow,

I = current, in amperes, passing through the voltameter;

x = polarization, in volts, on the metal partition ;

v = ohmic resistance of the voltameter, partition open.

Table I. was obtained with the old voltameter.

The results in Table II. were obtained with the new voltameter without leakage. The readings were taken after waiting two minutes for the current to become steady when a new plate was inserted, or the resistance changed for a new current-strength ; and in case of the thicker plates, where the time-change in the polarization was more pronounced and continued longer, five to ten minutes was allowed between readings, or in each case until the galvanometer indicated that the current had become about constant. Later tests given in another table show that this time-change of polarization, especially for thick plates, though at first rapid and then very slow, really continues some time.

TABLE I.

| | 30 per cent. sulphuric acid ; $v=1.6$ ohms. | | | | | | | |
Plate.	I.	x.	I.	x.	I.	x.	I.	x.
#1 gold.	0·1345	0·67	0·0665	0·33	0·0443	0·22	0·0222	0·12
#3 ,,	,,	0·78	,,	0·35	,,	0·26	,,	0·14
#4 ,,		0·50	,,	0·23	,,	0·17	,,	0·10
#5 ,,	,,	0·52	,,	0·24	,,	·0·17	,,	0·10
#6 ,,	,,	0·35	,,	0·16	,,	0·12	,,	0·05
#7 ,,	,,	0·0	,,	0·0	,,	0·0	,,	0·0

	5 per cent. H_2SO_4 ; $v=5.7$ ohms.					
#1 gold.	·078	1·42	0·0513	0·93	0·031	0·56
#3 ,,	,,	1·65	,,	1·11	,,	0·68
#4 ,,	,,	1·19	,,	0·79	,,	0·48
#5 ,,	,,	0·98	,,	0·67	,,	0·41
#6 ,,	,,	0·70	,,	0·46	,,	0·28
#7 ,,	,,	0·04	,,	0·02	,,	0·01

	Very dilute H_2SO_4 ; $v=101.7$ ohms.			
#1 gold.	·0047	1·67	0·0029	1·02
#3 ,,	,,	1·72	,,	1·07
#4 ,,	,,	1·21	,,	0·74
#5 ,,	,,	1·06	,,	0·67
#6 ,,	,,	0·70	,,	0·42
#7 ,,	,,	0·04	,,	0·03

TABLE II.   (Plate III.)

30 per cent. H_2SO_4 ; $v=1.1$ ohms.

#0 gold (·25 millim.), decreasing current.   Profuse gas.

I	0·175	0·093	0·061	0·037	0·018	0·009	0·004	0·002
x	2·83	2·37	2·03	1·28	0·67	0·33	0·17	0·09

Same, with increasing order of current.

x	2·66	2·34	2·15	1·45	0·71	0·35	0·16	0·09

Same, decreasing order again, without opening the circuit.

x	2·66	2·39	2·19	1·42	0·73	0·38	0·18	0·11

Same, after circuit was closed 2·5 hours.

x	2·66	2·56	2·33	1·53	0·79	0·39	0·20	0·12

Same, with increasing current again.

x	2·38	2·25	2·15	1·15	0·55	0·33	0·19	0·12

#1 gold.   Very long time between readings.   Gas.

x	2·36	2·39	2·29	2·27	2·18	2·10	1·90	1·02

#2 gold. Long time readings. Gas developed.

I	0·152	0·081	0·053	0·032	0·016	0·008		
x	3·05	2·96	2·98	2·86	2·79	2·72		

#3 gold. Gas developed.

I	0·184	0·093	0·061	0·037	0·019	0·009	0·004	0·002
x	2·57	2·42	2·00	1·41	0·83	0·37	0·15	0·07
x	2·29	2·28	2·11	1·41	0·83	0·37	0·15	0·07

#5 gold. No visible gas.

I	0·15	0·08	0·53	0·032	0·016	0·008
x	1·76	1·02	0·68	0·42	0·22	0·105

Same, reversed order without opening the circuit.

x	1·73	0·99	0·65	0·41	0·22	0·105

#6 gold. No visible gas.

I	0·1485	0·079	0·052	0·032	0·016	0·008
x	0·71	0·38	0·25	0·15	0·06	0·03

Same, reversed order.

x	0·71	0·38	0·25	0·15	0·06	0·03

#7 gold. No gas. Circuit closed 2·5 hours.

I ...... 0·15. No polarization.

#2 aluminium. No gas. No polarization.

#3 platinum. No gas. No polarization.

This solution, having been used a good deal with gold partitions, gave the following values for thick platinum and *gilded* the negative side of the partition :—

#1 platinum. Gas developed. Plate gilded.

I	0·175	0·093	0·061	0·037	0·0185	0·009	0·004	0·002
x	2·52	2·48	2·42	2·39	2·28	2·17	2·08	1·98

Same, reversed order of current.

x	2·59	2·52	2·44	2·39	2·28	2·18	2·09	1·98

#2 platinum. No visible gas.

x	0·89	0·53	0·36	0·26	0·15	0·108	0·085	0·07

Same, reversed order.

x	0·89	0·53	0·35	0·25	0·15	0·108	0·085	0·07

#1 silver. No gas.

x	0·87	0·46	0·42	0·26	0·20	0·12	0·09	0·08

Same, reversed order. Oxidized and very irregular.

x	0·53	0·28	0·31	0·15	0·15	0·12	0·096	0·08

#1 aluminium too much oxidized and too irregular to measure.

Fresh solution of H_2SO_4 ; 30 per cent. ; $v = 1·1$ ohms.

#1 platinum. Circuit closed four hours.

I	0·168	0·091	0·062	0·036	0·018	0·009	0·004	0·002
x	2·87	2·72	2·65	2·55	2·39	2·23	2·07	1·99

#2 platinum.

I	0·176	0·092
x	1·13	0·58

Table II. (*continued*).

3 per cent. H_2SO_4 ; $v = 6.3$ ohms.

#1 gold. Long time readings. Gas formed. Gold oxidized.

I	0.174	0.089	0.06	0.036	0.018	0.009	0.004	0.002
x	2.78	2.66	2.65	2.61	2.55	2.49	2.38	2.30

#2 gold. Long time readings. Gas.

I	0.156	0.091	0.061	0.037	0.018	0.009	0.004	0.002
x	2.67	2.59	2.61	2.56	2.49	2.43	2.43	2.28

#7 gold. Circuit closed 2.5 hours. No gas. x too small to measure.

KOH ; sp. gr. $= 1.11$.

#7 gold. No gas. No polarization.

NaCl ; sp. gr. $= 1.12$; $v = 5.5$ ohms.

#4 platinum. Very constant in very short time.

I	0.176	0.089	0.035
x	3.71	3.58	3.31

#7 gold. No gas. No polarization.

#2 aluminium. No gas. No polarization.

NaCl; sp. gr. $= 1.09$; $v = 6.24$ ohms.

#2 platinum. Very constant.

I	0.177	0.089	0.036
x	3.34	3.00	1.55

$CuSO_4$; sp. gr. $= 1.12$; $v = 24.5$ ohms.   Cu electrodes.

#1 platinum. Very constant, and for I $= 0.18$ gave $x = 2.19$.

#7 Au, #3 Pt, and #2 Al. No polarization. #1 Ag dissolved.

TABLE III.—Change of x with time.

I $= 0.175$. H_2SO_4, 30 per cent.; $v = 1.1$ ohms.

Time in minutes.	1.	3.	5.	10.	20.	30.	45.	60.	75.	100.	150.	220.
End electrodes.												
x	1.73	...	1.77	1.78	1.79	1.80	1.81	...	1.84	1.84		
Same, current reversed.												
x	1.44	...	1.76	1.77	1.78	...	1.81	...	...	1.84		
#1 platinum. Slightly gilded.												
x	1.91	2.08	2.14	2.21	2.24	2.30	2.33	2.35	2.36			
Same, current reversed.												
x	...	2.01	2.13	2.15	2.17	...	...	...	2.35	...	...	2.46

Table III. (*continued*).

Time in minutes.	1.	3.	5.	10.	20.	30.	45.	60.	75.	100.	150.	220.

♯2 platinum. No visible gas.

| x .... | 0·97 | 1·02 | ... | 1·07 | 1·09 | 1·10 | 1·11 | | | | | |

Same, current reversed.

| x .... | 0·96 | 1·02 | 1·06 | ... | 1·11 | 1·12 | 1·13 | | | | | |

♯0 gold. Oxidized. Gas.

| x .... | 2·14 | 2·25 | ... | 2·34 | 2·45 | 2·48 | ... | ... | ... | 2·53 | ... | 2·55 |

Same, current reversed.

| x .... | 1·94 | ... | 2·06 | 2·14 | 2·17 | 2·19 | 2·25 | 2·27 | 2·28 | | | |

♯4 gold. Gas, until the plate was eaten away by oxidation to a thin film, the oxide fell off, and polarization ceased.

| x .... | 2·37 | 2·43 | 2·49 | 2·55 | 2·63 | 2·66 | 2·70 | 2·54 | ... | 2·41 | 2·27 | 0·00. |

Fresh solution, 30 per cent. H_2SO_4.

Time in minutes.	1.	3.	5.	10.	20.	30.	45.	60.	75.	100.	150.	220.

♯1 platinum.

| x .... | 2·17 | 2·34 | 2·43 | 2·53 | 2·68 | ... | 2·85 | ... | ... | 2·92 | | |

Same, current reversed.

| x .... | 1·98 | 2·10 | 2·16 | 2·30 | 2·42 | 2·53 | 2·73 | ... | ... | ... | 2·87 | |

♯5 platinum.

| x .... | 2·37 | 2·45 | 2·53 | 2·65 | 2·74 | 2·83 | ... | ... | ... | 2·90 | | |

Same, current reversed.

| x .... | 1·99 | 2·08 | 2·12 | 2·24 | ... | ... | 2·59 | 2·63 | 2·67 | ... | ... | 2·68 |

♯3 Pt, ♯7 Au, and ♯2 Al, no polarization, so no time-change.

Solution, NaCl; sp. gr. = 1·09; $v = 6·24$ ohms.

Time in minutes.	1.	3.	5.	10.	20.

♯2 platinum. Gas.

| x .... | 2·97 | ... | 3·34 | 3·34 | 3·34 |

NaCl; sp. gr. = 1·12; $v = 5·5$ ohms.

Time in minutes.	1.	3.	5.	10.	20.

♯4 platinum. Gas.

| x .... | 3·51 | 3·56 | 3·67 | 3·71 | 3·72 |

Sample page of my note-book, showing how the observations were recorded and the tables obtained from them :—

♯7 gold in 30 per cent. H_2SO_4.

Zero of scale.	Scale-reading.	Deflexion, a.	Shunt, r_1.	Auxiliary resistance, R.	Branch resistance, r_2.	Sensibility for 1 ohm, σ.	Change of resistance, w.	Polarization, $Iw=x$. x.
337·5 336	940 939	603	1	28	1100	20	·1	·014
338 336	981 981	644	2	55	,,	12	·02	·016
338 337	974 973	636	3	85	,,	7·5	0	0
338 337	976 977	639	5	143	,,	5	0	0
338 337	984 983·5	646	10	287	,,	2·5	·2	·003
337 337	958·5 958·5	621	20	597	,,	1	1·0	·008

The ♯7 gold removed with a glass rod, not opening circuit.

Zero of scale.	Scale-reading.	Deflexion, a.	Shunt, r_1.	Auxiliary resistance, R.	Branch resistance, r_2.	Current, I.
336 336	940·5 942	605	1	28	1100	·1492
336 336	979·3 981·3	644·3	2	55	,,	·0795
336 336	972 972	636	3	85	,,	·0524
336·5 336	975 976	639	5	143	,,	·0316
336·5 336	981·5 982	645	10	287	,,	·0161
336 336	956·5 956·5	620	20	597	,,	·0078

The two readings in each case are for decreasing and increasing current respectively.

Then

$$i_2 = \gamma\alpha = {\cdot}000000224 \times 605 = {\cdot}0001355,$$

$$i_1 r_1 = i_2 r_2 = {\cdot}0001355 \times 1100 = {\cdot}14907 = i_1, \text{ since } r_1 = \mathrm{I},$$

$$\mathrm{I} = i_1 + i_2 = {\cdot}1492 \text{ ampere.}$$

$$w = \mathrm{R} - \mathrm{R}' = \text{two scale-divisions} = \frac{2}{20} = {\cdot}1.$$

$$(20 = \sigma = \text{scale-divisions for one ohm change of R.})$$

$$\mathrm{I}w = x = 0{\cdot}014 \text{ volt.}$$

In this manner, from such a table in the note-book, one line in Table II. was obtained. The sample-page of my notes for ♯7 gold was selected to illustrate the method of observation and reduction, because it also serves as a fair sample of many efforts to measure quantitatively the polarization on gold-leaf in good-conducting (30 %) H_2SO_4. One has only to look at the time-variation of the polarization on the end electrodes to be able to account for such slight variations from zero as occur here (see Table III.). Having become satisfied from many such series of observations that there was no measurable polarization on gold-, aluminium-, and platinum-foil for currents as strong as used, I then adopted an efficient method of testing them for polarization in various solutions, viz., to allow the strongest current to flow through the plate long enough to become constant, and then, without opening the circuit, to remove the metal partition with a glass rod and simply observe whether there was a change of deflexion of the galvanometer. On this method of observation is based the statement under the tables that for these thinnest partitions there is no polarization for the currents used. The qualitative results of Table I., with the old voltameter, seem to indicate pretty clearly a small polarization on ♯7 gold in very dilute (badly-conducting) acid. A preliminary test in the new voltameter of water containing only a few drops of acid, using gold-leaf as partition, gave sufficient polarization to develop visible gas.

From Table IV. (p. 198) it seems that for a given current-strength the polarization is fairly proportional to the square of the thickness of the partition for plates near the lower critical thickness. The last column shows this ratio as worked out for ♯5 and ♯6 gold.

TABLE IV.   (Pl. IV. fig. 1.)

Relation of Polarization to Thickness ; 30 per cent. H_2SO_4 ; gold plates.

Thickness in millimetres } ...		# 6. 0·00038	# 5. 0·00059.	# 3. 0·0043.	Ratio. $d^2 : x.$
Current. I = ·01	x ...	·04	·09	0·40	441 : 484
I = ·02	x ...	·09	·26	0·77	1274 : 1081
I = ·03	x ...	·13	·39	1·13	1911 : 1694
I = ·04	x ...	·19	·50	1·48	2450 : 2299
I = ·05	x ...	·28	·76	2·02	3724 : 3388
I = ·10	x ...	·47	1·23	2·35	6027 : 6681
I = ·15	x ...	·71	1·76	2·35	8624 : 8591

We may now briefly summarize the experimental observations :—

(1) The polarization on a gold-leaf partition in good-conducting H_2SO_4 is zero, or too small to detect with our apparatus, for the range of current used.

(2) The " critical thickness " in good-conducting solutions of H_2SO_4, $CuSO_4$, and NaCl is *greater* than ·00009 millim. for gold ; ·00015 millim. for platinum ; and ·0005 millim. for aluminium, under the above conditions.   It is *less* than ·0004 millim. for gold ; ·002 millim. for Pt ; and ·002 for Ag.

(3) The " upper critical limit " of thickness under these conditions seems to be about ·004 millim., rather less than ♯3 gold.

(4) Tables I., II., and III. all point to the conclusion that between the " critical limits " of thickness the polarization for a given current increases with the thickness.

(5) Table II., showing relation of polarization to current, expresses two interesting facts :—(*a*) That the polarization on " thick " plates is about the same, in this voltameter, for all currents between ·2 amp. and, say, ·01 amp., provided time enough be allowed in each case for the current to become constant: *i. e.* between the upper limit of current at which the development of gas is so profuse as by mechanical obstruction and irregular escape to interfere, and the lower limit, at which the formation of gas is no faster than it can be

dissipated. (*b*) Quite different is the case for "thin" plates, where, within the limits of current and thickness prescribed, the polarization is dependent upon the current, and gives for each thickness a different curve, or rather straight line, for they are all straight lines converging to the origin, and differing only in *slope.* The current-strength at which the polarization on very thin plates would reach a maximum is far above that used, being, perhaps, expressed in amperes instead of tenths and hundredths.

By *thick* plates are defined those above the "upper critical limit;" by *thin* plates those below this limit of thickness.

(6) Inspection of Table III., which gives the time-change of the polarization, will show a similar distinction between "thick" plates and "thin" to that noted in the last paragraph, viz., that for thick plates the change is considerable and continues slowly for hours; for thin plates, the change of polarization with time is both less pronounced and extends over much less time.

(7) It was noted, especially in the case of $CuSO_4$ as electrolyte, that there was polarization on gold-leaf if the gold exposed contact with the solution some distance beyond the edge of the hole in the glass plate to which it was sealed. Thus in $CuSO_4$, for the stronger current used there was a symmetrical deposit of Cu, decreasing in thickness from the outside toward the centre, and vanishing at a small distance from the edge of the hole, this distance being less the stronger the current. If only one corner was left exposed, the Cu was deposited there. This phenomenon was further tested by bending a thick strip of aluminium 4 centim. long into the shape of a narrow U and simply hanging this U in the *open* hole of the glass partition, in $CuSO_4$, and closing the circuit on the voltameter; the two ends of the metal strip being thus in contact with the $CuSO_4$ on opposite sides of the glass, two centim. from the edge of the opening, there was decided deposit of Cu on one end and escape of oxygen from the other end.

(8) In $CuSO_4$ all the plates except those below the critical thickness were destroyed by oxidation. ♯1 silver was destroyed in less than one minute. Of course gold and silver above the critical thickness could not be used in NaCl because of chemical action, though the thinnest plates were quite unaffected. Only the ♯7 gold was tested in KOH, as it dissolved the sealing-wax.

(9) Thick plates of gold were strongly oxidized in H_2SO_4, especially with strong currents. Thin gold plates were apparently only oxidized under action of strong or **long**

continued currents. Compare Tables II. and III. Silver was even more easily oxidized than gold. Aluminium was so intensely oxidized by the current that no satisfactory measurements could be made for this metal, though the thin foil was unaffected.

(10) With H_2SO_4 as electrolyte, after a thick plate of pure gold had been used as partition for the time-change of Table III., the end kathode was found to be gilded. A thick Pt plate being then substituted for the gold in the same solution for the results of ♯1 Pt in Table III., the Pt partition was found on removal to be gilded. The polarization for ♯1 Pt in this case was somewhat less than for the same Pt after both it and the end electrodes had been thoroughly cleansed, the electrodes re-platinized, and a fresh solution made.

(11) The polarization in $CuSO_4$, using Cu electrodes, reached a maximum almost immediately and remained very constant. The maximum polarization for thick Pt in $CuSO_4$ was hardly 75 per cent. of that for the same in H_2SO_4. In NaCl the polarization became constant very quickly also, but its value was decidedly greater, especially on thin plates, than in H_2SO_4; though the same distinctive behaviour of thick and thin plates maintained.

(12) In H_2SO_4 of different concentrations the maximum polarization for a partition was of the same order of magnitude; but its value for very weak currents was decidedly greater in weak solutions than for the same current in stronger solutions, up to 30 per cent. This shows itself especially with thin plates, and also in the shorter time required for thick plates to reach a maximum polarization with weak currents. The greater change in temperature and the greater change in concentration of weak solutions may account for this. For currents between 0·1 and 0·2 ampere, the polarization on the end electrodes was,

$$\begin{array}{llll} \text{for } H_2SO_4 & . & . & . & 1\cdot84 \\ \text{,, NaCl} & . & . & . & 1\cdot98 \\ \text{,, } CuSO_4 & . & . & . & 0\cdot00, \end{array}$$

with Cu electrodes, though if the current-density was too great or the time long, the anode would oxidize and become irregular. C. Fromme, in a paper " Ueber das Maximum der galvanischen Polarization von Platinelektroden in Schwefelsäure " (*Annalen d. Physik u. Chemie*, xxxiii. pp. 80–126), states that the maximum polarization varies both with the concentration and the relative size of the electrodes, the extreme limits being given as 1·45 to 4·31 volts—the minimum polarization coinciding with maximum conductivity.

His method for measuring polarization was somewhat similar to that used in this work. As bearing upon "the change of polarization with time" I would refer especially to the investigation of Dr. E. Root upon this subject, discussed by Prof. von Helmholtz, *Wisch. Abh.* vol. i. p. 835. These experiments by Dr. Root seem to prove clearly that the liberated ions penetrate deeply into the electrode, even when liberated upon but one side of it, as in this case. I take great pleasure in expressing here my thanks and deep obligation to Professor A. Kundt and Dr. L. Arons for their kind sympathy and direction in this work.

Physical Laboratory, Univ. of Berlin,
    August 1892.

XV. *A Potentiometer for Alternating Currents.* By JAMES SWINBURNE[*].

ARGUMENT.

A direct pressure is balanced against an alternating pressure by means of a differential electrometer with single-fibre suspension, a null method being employed. An alternating and a direct current are similarly compared by means of a differential dynamometer with the controlling spring removed.

ONE of the chief difficulties in the way of the accurate measurement of alternating pressures and currents arises in the calibration of the instruments. Some of the alternating-current instruments, such as those on the electro-dynamometer principle, give the same reading whether a direct or alternating current is used; and electrometers and some forms of electromagnetic instruments with soft iron cores are also adapted equally well for direct and alternating-current work. This is not the case, however, with a large class of instruments, and the only method at present available for calibrating such instruments is comparing them with another instrument which has been calibrated by means of a direct current. Such a practice allows errors to creep in. No careful electrician would trust to direct-current instruments calibrated second-hand, and accuracy is just as important in alternating-current work. In addition to this, the collection of cells and resistances which are now included under the name "potentiometer" is exceedingly useful in any laboratory where it can be permanently set up, as it measures currents and pressures throughout an enormous

range with an accuracy that is quite unattainable by means of any other forms of voltmeter or ampere-meter. It is therefore of the highest scientific importance to be able to extend the potentiometer method into alternating-current work, so that comparisons can be made directly with a standard cell.

In October 1891[*] I described two forms of alternating-current so-called ohmmeter. These instruments measured either a quantity R such that E^2/R was the power when E was the effective or virtual pressure, or a quantity r such that Cr^2 was the power when C was the virtual or effective current. Of course in a circuit with capacity or self-induction, R and r are not equal. One form of alternating ohmmeter was electrostatic, the other electromagnetic. The electrostatic ohmmeter can be coupled up in such a way as to compare two pressures, and one of these may be alternating and the other direct. The electrostatic instrument has the advantage over the electromagnetic in requiring only one connexion to the moving system, or needle, and that connexion has not to carry any appreciable current. The needle may therefore be suspended by means of a single silk fibre, connexion being made through a hanger dipping into water, and this hanger may end in a vane to make the instrument dead-beat. As the ohmmeter does not need any torsional control, but should be, on the contrary, as free as possible, this form of instrument can be made exceedingly sensitive. For potentiometer work it is best not to use the instrument for giving the ratio of two electromotive forces, but to design it as a differential galvanometer which shows whether the pressures are equal or not.

Fig. 1.
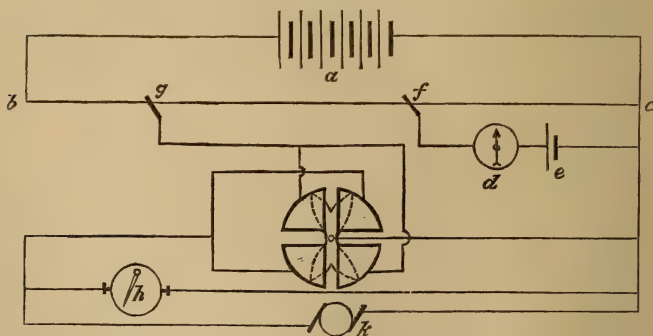
The disposition of the whole apparatus is shown diagrammatically in fig. 1. In this scheme a is a battery maintaining

a current in the resistance bc, which is regulated by an adjustable resistance so that the standard cell e is balanced when its contact f is touched down at the mark corresponding to its electromotive force at the temperature at which it stands ; k is an alternating dynamo, and h is the alternating voltmeter to be calibrated. The differential electrometer is connected up as shown. The double fishtail-shaped needle is pulled one way by a force varying as the square of the direct electromotive force, and the other way by a force varying as the square of the alternating pressure. The fishtail shape is necessary to ensure that the needle is in stable equilibrium when the forces are equal. Fig. 1 is, of course, a mere diagram. Resistance-coils for adjustment are left out, and bc is shown as a stretched wire, whereas it is made up of resistance-coils. As to sensitiveness, it depends on the construction of the electrometer ; but, as already explained, there is no controlling force except that due to the suspending fibre. Take as an example an instrument that will indicate one volt when there is no pressure on the other side : it will admit of the comparison of two pressures of approximately 100 volts within one in ten thousand ; and it will serve for comparing 2000 volts within one in four million. To find the true zero of the instrument the four quadrants are connected together. The key for making this connexion is not shown.

One of the great advantages of the potentiometer method in direct-current work is the ease with which large currents can be measured by the fall of potential over very small resistances. As the electrometer must be used idiostatically in alternating work it is not sensitive to very small pressures; and the method given is, unfortunately, useful only for pressure measurements. Accurate current measurements can be taken by the use of a differential dynamometer. This instrument has two fixed and one moving coil. The direct circuit is through one fixed and the alternating through the other fixed coil, and both circuits are led through the moving coil. The controlling spring is removed. This method is somewhat more complicated than in the case of pressure, and mercury contacts are necessary. The arrangement is shown in fig. 2. The battery, a, supplies a direct current, which is measured by the fall of potential over the low resistance, b, and which passes in one of the fixed coils, c, and the moving coil, d. The alternating-current circuit is led through the circuit, f, whose current is to be measured, and through the other fixed coil, e, and the moving coil, d. There is a slight error due to the whole of the alternating circuit being in shunt to the moving coil considered as part of the direct-current circuit, and *vice versâ* ; but this is very minute. If

c and *e* are wound close together so that there is no appreciable time-lag in any current induced in *c* by *e*, the small error due to the mutual induction of these coils cancels out.

Fig. 2.
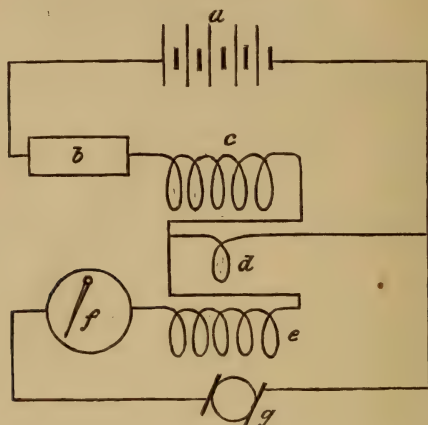
Of course a double dynamometer might be used, but then four mercury connexions are needed. It is not unlikely that a method with no mercury contacts can be made available, and greater accuracy could then be attained.

XVI. *Calculation of the Magnetic Field of a Current running in a Cylindrical Coil.* By Professor G. M. MINCHIN, *M.A.*[*]

LET there be a series of very close circular currents running in the same sense and lying on a right cylinder of radius *a* whose axis is OO′ (fig. 1), and let it be required to find the magnetic potential of this system at any point, P, in space.

Replace each of these circular currents by its equivalent magnetic shell, which we shall take as a uniform circular plate coinciding with the aperture of the circle. Supposing the currents to circulate in the sense ACB, the upper surface of each plate (as seen in the figure) will be positive and the lower negative. Each circle being touched all round by the one below it, the negative surface of any plate will coincide with the positive of the one next below it; so that we shall be left with a terminal positive plate, ACB, and a terminal

negative plate, A'C'B', as the approximate equivalent of the given coil of wire. We shall now calculate the potential

Fig. 1.
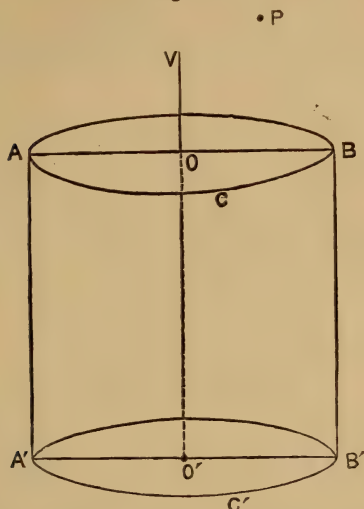
produced at any point, P, by a uniform thin plate represented by AQB (fig. 2), the surface-density of attracting matter on this plate being m.

Fig. 2.
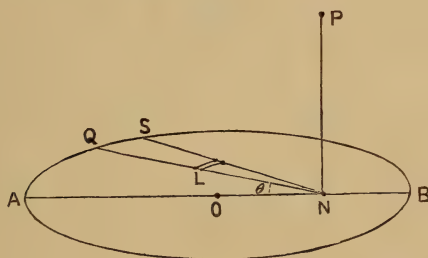
Of course it is well known that this potential can be exhibited by a series of Zonal Harmonics proceeding by powers, positive or negative, of the ratio $\dfrac{OP}{a}$, where O is the centre of the plate and a its radius, according as P is near O or distant from it ; but when OP is not *very* much greater or *very* much less than a, the series is inconvenient, owing to the enormous number of terms that have to be taken to give a good approximation.

Hence we shall not use Spherical Harmonics.

Let PN be the perpendicular on the plate from P; let AB be the diameter in which it is cut by the plane through the axis of the plate and P; let Q, S be two very close points on the circumference, NQ making the angle θ with NA. Then we shall suppose the plate broken up into triangular strips such as QNS, and calculate the potential of each strip at P.

Let L be any point on NQ, let $NL = \xi$; then the potential of the element $m\xi d\xi d\theta$ at P is $\dfrac{m\xi d\xi d\theta}{LP}$, or $md\theta \dfrac{\xi d\xi}{\sqrt{z^2 + \xi^2}}$, where $PN = z$. If $NQ = r$ we find by integration that the potential produced by the strip QNS is

$$md\theta(\sqrt{r^2 + z^2} - z), \quad \ldots \ldots \ldots \quad (1)$$

and the potential, V, of the whole plate is

$$2m \int (\sqrt{r^2 + z^2} - z) d\theta. \quad \ldots \ldots \quad (2)$$

Now if, as in the figure, the point N falls within the plate, the limits of θ are 0 and π; if N falls on the edge of the plate, at B, the limits are 0 and $\dfrac{\pi}{2}$; and if it falls outside the plate, the limits are 0 and 0. Taking θ as the independent variable would, then, give us three different expressions for V, according to the position of N; and hence we must choose a more convenient variable than θ. Let ϕ be the angle QOA, and change the expression (2) into one in which ϕ is the independent variable. We shall then have

$$r^2 = a^2 + x^2 + 2ax \cos \phi; \quad \tan \theta = \frac{a \sin \phi}{x + a \cos \phi};$$

so that

$$V = 2ma \int_0^\pi \frac{\sqrt{a^2 + x^2 + z^2 + 2ax \cos \phi} - z}{a^2 + x^2 + 2ax \cos \phi} (a + x \cos \phi) d\phi;$$

or if we put $D = a^2 + x^2 + 2ax \cos \phi$,

$$\frac{V}{m} = \int_0^\pi \frac{\sqrt{z^2 + D} - z}{D} (D + a^2 - x^2) d\phi$$

$$= \int_0^\pi \sqrt{z^2 + D} \, d\phi + (a^2 - x^2) \int_0^\pi \frac{\sqrt{z^2 + D}}{D} d\phi - z \int_0^\pi \left(1 + \frac{a^2 - x^2}{D}\right) d$$

Now

$$(a^2 - x^2) \int_0^\pi \frac{d\phi}{D} = \pi;$$

so that

$$\frac{V}{m} = -2\pi z + \int_0^\pi \sqrt{z^2 + D}\, d\phi + (a^2 - x^2) \int_0^\pi \frac{\sqrt{z^2 + D}}{D}\, d\phi$$

$$= -2\pi z + \int_0^\pi \sqrt{z^2 + D}\, d\phi + (a^2 - x^2) \int_0^\pi \frac{d\phi}{\sqrt{z^2 + D}}$$

$$+ (a^2 - x^2) z^2 \int_0^\pi \frac{d\phi}{D \sqrt{z^2 + D}}. \quad . \quad (3)$$

Again, if we put $\phi = 2\omega$, we have

$$D = (a + x)^2 - 4ax \sin^2 \omega\ ;$$

and if the distances PA, PB are denoted by ρ, ρ', respectively, we have

$$4ax = \rho^2 - \rho'^2,$$

so that

$$z^2 + D = \rho^2 - (\rho^2 - \rho'^2) \sin^2 \omega.$$

Let

$$k^2 = 1 - \frac{\rho'^2}{\rho^2}\ ; \quad k'^2 = \frac{\rho'^2}{\rho^2}\ ; \quad \Delta\omega = \sqrt{1 - k^2 \sin^2 \omega}. \quad . \quad (4)$$

Then (3) becomes

$$= -2\pi z + 2\rho E + \frac{2}{\rho}(a^2 - x^2)K + 2\frac{z^2}{\rho}\frac{a - x}{a + x} \cdot \int_0^{\frac{\pi}{2}} \frac{1}{1 - \dfrac{4ax}{(a + x)^2}\sin^2 \omega} \cdot \frac{d\omega}{\Delta\omega}, \quad (5)$$

where E and K are the complete elliptic integrals of the second and first kinds with modulus k.

The integral in (5) is the complete elliptic integral of the third kind with modulus k and parameter $-\dfrac{4ax}{(a + x)^2}$. This parameter is numerically greater than the modulus; and we shall find it convenient to convert the integral into one in which the parameter is less than the modulus by the well-known rule that a function with parameter n can be converted into one with parameter $\dfrac{k^2}{n}$. If the angles PBA and PAB are denoted by θ and θ', respectively, we see that n, the parameter in (5), is $-\dfrac{k^2}{\cos^2 \theta'}$; so that the new parameter will be simply $-\cos^2 \theta'$.

Now we have the general result that

$$\Pi(n, \epsilon) + \Pi\left(\frac{k^2}{n}, \epsilon\right) = \frac{1}{\sqrt{\alpha}} \tan^{-1}\left(\frac{\sqrt{\alpha}\tan \epsilon}{\Delta\epsilon}\right) + K(\epsilon),$$

where ϵ is the amplitude of each of the two functions of the third kind (denoted by Π), and $\alpha = (1+n)\left(1+\dfrac{k^2}{n}\right)$. Hence for complete functions $\left(\epsilon = \dfrac{\pi}{2}\right)$ we have

$$\Pi(n) + \Pi\left(\frac{k^2}{n}\right) = \frac{\pi}{2\sqrt{\alpha}} + K.$$

But here

$$\alpha = \left(1 - \frac{k^2}{\cos^2\theta'}\right)\sin^2\theta' = \left(\frac{a-x}{a+x}\right)^2 \cdot \frac{z^2}{\rho^2};$$

so that

$$\Pi\left(-\frac{k^2}{\cos^2\theta'}\right) = \frac{\pi}{2}\frac{\rho}{z}\frac{a+x}{a-x} + K - \Pi(-\cos^2\theta'), \quad . \quad . \quad (6)$$

and (5) becomes

$$\frac{V}{m} = -\pi z + 2\rho E + 2\rho\frac{a-x}{a+x} \cdot K - 2\frac{z^2}{\rho}\frac{a-x}{a+x}\Pi(-\cos^2\theta', k). \quad (7)$$

This expression holds without ambiguity for all positions of the point P, and it shows that for all points

on the axis, OV, of the plate, $\quad . \quad \dfrac{V}{m} = 2\pi(\rho - z), . \quad . \quad (8)$

on the perpendicular through B, $\quad \dfrac{V}{m} = 2\rho E - \pi z, . \quad . \quad (9)$

in the plane, between O and B, . $\quad \dfrac{V}{m} = 2\rho E + 2\rho'K, . \quad (10)$

in the plane, beyond B, $\quad . \quad . \quad . \quad \dfrac{V}{m} = 2\rho E - 2\rho'K ; . \quad (11)$

so that the points, occupying any of these positions, at which V has any assigned value can be easily found. Thus, to find the point on OV at which $\dfrac{V}{m}$ has the value C, we have for this point

$$\rho = z + \frac{C}{2\pi}.$$

Hence draw below AB, parallel to it and at the distance $\dfrac{C}{2\pi}$, a right line, meeting VO produced in O′; then the perpendicular to AO′ at its middle point meets OV in the required point.

Now every complete elliptic integral of the third kind can be expressed in terms of complete and incomplete

functions of the first and second kinds. Thus, for a complete function with the parameter $-m$ it is known that, if we put $m = -k'^2 \sin^2 \epsilon$,

$$\Pi(-m, k) = K + \frac{\Delta'_\epsilon}{k'^2 \sin \epsilon \cos \epsilon} \left\{ \frac{\pi}{2} + KK'_\epsilon - KE'_\epsilon - EK'_\epsilon \right\}, \quad (12)$$

where Δ'_ϵ stands for $\sqrt{1 - k'^2 \sin^2 \epsilon}$, and K'_ϵ, E'_ϵ stand for incomplete functions of the first and second kinds with modulus k' and amplitude ϵ.

In the present case,

$$m = \cos^2 \theta', \quad k' = \frac{\rho'}{\rho} = \frac{\sin \theta'}{\sin \theta};$$

$\therefore \epsilon = \theta$, and

$$\Pi(-\cos^2 \theta', k) = K + \frac{\cos \theta'}{k'^2 \sin \theta \cos \theta} \left\{ \frac{\pi}{2} + KK'_\theta - KE'_\theta - EK'_\theta \right\}; \quad (13)$$

so that (7) becomes

$$\frac{V}{2m} = z\{KE'_\theta + EK'_\theta - KK'_\theta - \pi\} + \rho E + \rho' \cos \theta \cos \theta' \cdot K. \quad (14)$$

It is evident that we may define the position of any point, P, in the plane of the figure by means of the two coordinates k and θ. Thus we have

$$\rho = \frac{2a}{\Delta'_\theta + k' \cos \theta},$$

$$\cos \theta' = \Delta'_\theta,$$

$$z = k' \rho \sin \theta, \quad \rho' = k' \rho.$$

Hence

$$\frac{V}{4m} = \frac{a}{\Delta'_\theta + k' \cos \theta} \{ E + k' \sin \theta \, (KE'_\theta + EK'_\theta - KK'_\theta - \pi) + k' \cos \theta \cdot K \Delta'_\theta \}. \quad (15)$$

This, then, is the expression for the potential at any point in terms of the coordinates (k, θ) of the point. In particular, it gives the value (9) for any point on the perpendicular through B to the plate, since for such a point $\theta = \frac{\pi}{2}$, and then the coefficient of $k' \sin \theta$ within the brackets is equal to $-\frac{\pi}{2}$, by Legendre's well-known relation between the complete complementary functions, viz.,

$$KE' + EK' - KK' = \frac{\pi}{2},$$

whatever the modulus k may be.

From (14) we can derive an expression for the conical angle subtended at any point, P, in space by a circle, *i. e.*, for the magnetic potential due to a current coinciding with the circle. It is well known that this conical angle is numerically equal to the component of the attraction, perpendicular to the plate, at P due to a uniform circular plate coinciding with the aperture of the circle—a result which is evident from the principle that the current can be replaced by a magnetic shell, or thin plate, the upper and lower surfaces of which are, of course, of opposite signs. But the resultant potential of these two indefinitely close plates is the difference between the value of V in (14) and the value which (14) assumes when $z + \Delta z$ is substituted for z; that is, the magnetic potential at P due to the current is $-\dfrac{d\mathrm{V}}{dz} . \Delta z$, and the strength of the magnetic shell is $m . \Delta z$, which is i, the current in the circle; so that the magnetic potential is i multiplied by minus the differential coefficient of the right-hand side of (14) with respect to z.

Denote the function $\pi + \mathrm{K}\mathrm{K}' - \mathrm{K}\mathrm{E}'_\theta - \mathrm{E}\mathrm{K}'_\theta$ by the symbol Λ_θ, and for simplicity in the differentiation with respect to z (x being constant) write (14) in the form

$$\frac{\mathrm{V}}{2m} = -z\Lambda_\theta + \rho\mathrm{E} + (a^2 - x^2)\frac{\mathrm{K}}{\rho} . \quad . \quad . \quad (16)$$

Now

$$\left.\begin{array}{ll}
\dfrac{d}{dz} = -\dfrac{kk'}{\rho}\sin\theta; & \dfrac{dk'}{dz} = \dfrac{k^2}{\rho}\sin\theta; \\[2ex]
\dfrac{d\rho}{dz} = k\sin\theta; & \dfrac{d\theta}{dz} = \dfrac{1}{k'\rho}\cos\theta;
\end{array}\right\} \quad . \quad . \quad (17)$$

and, regarding P as determined by the coordinates (z, x) instead of (k, θ), we have

$$\frac{d}{dz} = \frac{dk}{dz} . \frac{d}{dk} + \frac{d\theta}{dz} . \frac{d}{d\theta};$$

but

$$\frac{d\Lambda}{dk} = \frac{\mathrm{K} - \mathrm{E}}{k}\frac{\sin\theta\cos\theta}{\Delta'_\theta},$$

$$\frac{d\Lambda}{d\theta} = \frac{\mathrm{K}k'^2\sin^2\theta - \mathrm{E}}{\Delta'_\theta};$$

therefore

$$\frac{d\Lambda}{dz} = -\frac{1}{k'\rho}\mathrm{E}\Delta'_\theta\cos\theta,$$

and we find $\dfrac{d}{dz}$ of the right-hand side of (16) equal to $-\Lambda_\theta + k'\mathrm{K}\sin\theta$; so that if Ω is the conical angle subtended at P by the circle, or the magnetic potential per unit current in the circle, we have the very simple expression

$$\Omega = 2\Lambda_\theta - 2k'\mathrm{K}\sin\theta. \quad . \quad . \quad . \quad (18)$$

Again, supposing that the depth, OO' (fig. 1), of a coil consisting of a single series of circular currents is small compared with the distance of the point P from any part of it, the two terminal plates, ACB, A'C'B' may be considered as close together, and the potential of the coil at P is the value of V in (16) minus the value obtained by putting $z+h$ for z, where $h = \mathrm{OO}'$. Hence the potential in such a case is $-mh\Omega$, i. e., *at any point in space whose distance from every part of a coil is great compared with the depth of the coil, the potential is*

$$2mh(\Lambda_\theta - k'\mathrm{K}\sin\theta). \quad . \quad . \quad . \quad . \quad (19)$$

The modulus k which appears in these equations, being $\left(1 - \dfrac{\rho'^2}{\rho^2}\right)^{\frac{1}{2}}$, is constant at all points for which $\dfrac{\rho'}{\rho}$ is constant; i. e., at all points on any circle which cuts that described on AB as diameter orthogonally. The circles which cut this

Fig. 3.
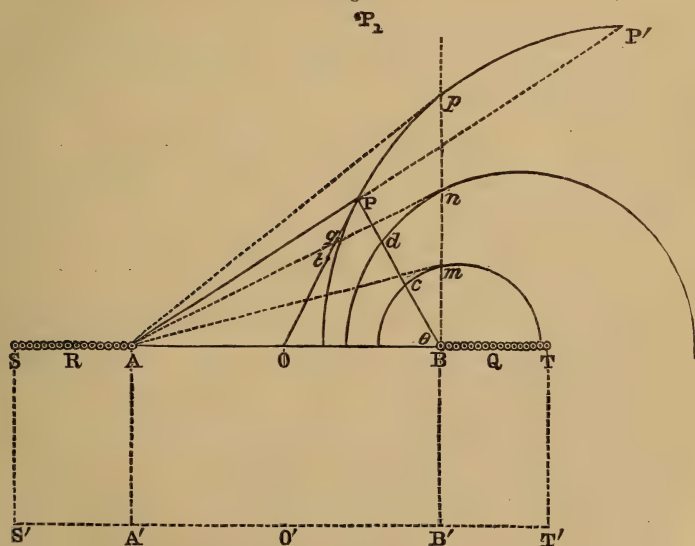
latter orthogonally, having their centres on AB, are most readily drawn by joining A to points, $m, n, p, \ldots$ (fig. 3) on

the perpendicular at B to AB, and drawing perpendiculars at $m, n, p, \ldots$ to Am, An, Ap, $\ldots$; the points of intersection of AB produced with these perpendiculars are the centres of the circles. If C is the centre of the orthogonal circle through m, we know that the constant, $1 - \dfrac{\rho'^2}{\rho^2}$, on this circle is $\dfrac{\mathrm{AB}}{\mathrm{AC}}$, *i. e.*, $\cos^2 m\mathrm{AB}$. Hence if $m\mathrm{AB} = \beta$, we have

$$k = \cos \beta; \qquad k' = \sin \beta. \quad . \quad . \quad . \quad (20)$$

The field due to the plate AB is most readily mapped out by describing a large number of very close circles of the orthogonal system for a regular gradation of the values $m\mathrm{AB}$, $n\mathrm{AB}$, $p\mathrm{AB}$, $\ldots$ of β, drawing a line BP in the assigned direction θ, and from Legendre's tables of Elliptic Integrals taking out the values of K, E, K'_θ, E'_θ.

The properties of the orthogonal circles lead to some simple results with regard to potentials. Thus, if any line, AP, is drawn from A cutting any circle of the series in P and P′, the lines joining P and P′ to B are equally inclined to AB, *i. e.*, $\angle \mathrm{ABP}' = \pi - \theta$.

Now if in Λ_θ we put $\pi - \theta$ for θ, we have, in virtue of Legendre's relation between complete complementary integrals, $\Lambda_{\pi-\theta} = \pi - \Lambda_\theta$, *i. e.*,

$$\Lambda_{\pi-\theta} + \Lambda_\theta = \pi. \quad . \quad . \quad . \quad . \quad (21)$$

Hence, from (18), if Ω, Ω' are the conical angles subtended at P, P′ respectively by the circle (or plate) AB, we have the remarkable relation

$$\Omega + \Omega' = 2\pi - 4k'\mathrm{K} \sin \theta. \quad . \quad . \quad . \quad (22)$$

Again, if V, V′ are the potentials at P, P′ due to the plate, we have from (15)

$$\frac{\mathrm{V}}{\mathrm{AP}} + \frac{\mathrm{V}'}{\mathrm{AP}'} = 2m(2\mathrm{E} - \pi k' \sin \theta), \quad . \quad . \quad (23)$$

a result which enables us to lay down the field at all points to the right of the perpendicular Bp when the field to the left of Bp is known.

Supposing now that instead of a single wire of diameter AB, we have a series of wires forming a coil contained between the diameter AB and the diameter ST, *i. e.*, the breadth of the coil is BT or AS ; then in calculating the potential at P we shall have to find the potentials due to a series of circular plates, each of surface-density m, and to add these potentials together. But observe that the potential at P due

to any plate, AB, of radius a is of the form

$$a \cdot \phi(k, \theta), \quad \ldots \quad \ldots \quad (24)$$

where $\phi(k, \theta)$ is the coefficient of a in (15), and $\phi(k, \theta)$ is a function of θ and θ', the angles PAB and PBA. Hence if we take a plate of radius OQ, and from B draw Bq parallel to QP and meeting OP in q, the potential of this plate at P is to the potential of the plate AB at q as OQ is to OA; for, if AR = BQ, the angles qBA and qAB are equal, respectively, to PQR and PRQ. Hence, if r = OQ and V_q is the potential at q due to the plate AB (of radius a), the resultant potential at P due to the series of plates of radii extending from OB to OT is

$$\frac{1}{a} \Sigma r \cdot V_q, \quad \ldots \quad \ldots \quad (25)$$

the points q on OP ranging from t to P, where Bt is parallel to PT.

Of course any plate of the series may be taken instead of AB as the reference plate.

Thus, *the resultant potential, due to all the plates, is calculated from values of the potential of any one plate at a series of points ranged along the radius vector* OP.

Pass now to the consideration of the practical problem in hand, viz., the potential at P due to a coil of depth OO′, *i. e.*, we have to consider the whole of the spaces BTT′B′ and ASS′A′ filled with wire traversed by a current of strength i. We have already seen that we have to subtract from the potential at P due to a series of uniform attracting plates, each of surface-density m, ranging from the radius OB to the radius OT, the potential at P due to the lower series, each of surface-density m, and ranging from radius OB′ to radius OT′. It merely remains to express m in terms of current-density. If C is the total quantity of current traversing (at right angles to the plane of the paper) a unit area (square centimetre) of the space BTT′B′, the quantity flowing in a filament of depth dy and breadth dr is C$dy dr$. Now this filament is replaced by the magnetic shell of radius r and thickness dy; and since we know that the strength of the shell is equal to the current in the filament, we have $m \cdot dy = \mathrm{C} dy dr$, $\therefore m = \mathrm{C} dr$; hence (25) becomes, from (15),

$$4\mathrm{C} \int r \cdot \phi(k, \theta) dr, \quad \ldots \quad \ldots \quad (26)$$

which is the potential due to the upper series of plates, OB, ... OT.

This quantity may be graphically represented and calculated as follows. Let a very close series of curves representing

a series of constant values of the function $\phi(k, \theta)$ for the plate AB be drawn ; draw OP, and at each point, T, Q, ... B, of the breadth BT of the coil draw an ordinate, Th, Qg, ... Bf (fig. 4), equal to the product of r and the

Fig. 4.
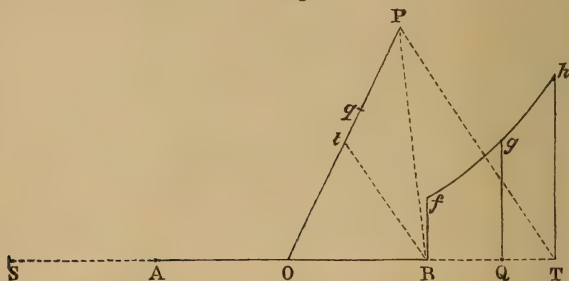
value of $\phi(k, \theta)$ at the corresponding point, t, q, ... P, of the line OP : these ordinates will form by their extremities a curve, hg ... f, the area of which multiplied by four times the current-density in the space occupied by the coil is the potential at P due to the upper series of plates, OB, OQ, ... OT.

Now if we take the point P_1 such that PP_1 is equal and parallel to OO', the depth of the coil, the potential at P due to the lower series of plates, OB', ... OT', is equal to that at P_1 due to the upper series. Hence, if A and A_1 are the areas of the curve hg ... f and the corresponding curve for the point P_1, the total potential at P due to the complete coil is

$$4C(A - A_1). \quad . \quad . \quad . \quad . \quad . \quad (27)$$

The curve hgf passes, of course, through the point O ; and when the line OP coincides with the axis, OO', of the coil, the curve is an hyperbola ; for, in this case

$$\phi(k, \theta) = \frac{\pi}{2} \cdot \frac{1 - \sin\theta}{\cos\theta},$$

and $r = $ OP $\cot\theta$.

We may, if we please, express r in terms of (k, θ), and draw the curve hgf by a different rule. Thus,

$$r = \text{OP} \cdot \frac{\Delta'_\theta + k' \cos\theta}{\sqrt{(\Delta'_\theta - k' \cos\theta)^2 + 4k'^2 \sin^2\theta}},$$

and we can make the ordinate of the curve equal to

$$\text{OP} \cdot \frac{\text{E} - k' \sin\theta \cdot \Lambda_\theta + k'\text{K} \cos\theta \cdot \Delta'_\theta}{\sqrt{(\Delta'_\theta - k' \cos\theta)^2 + 4k'^2 \sin^2\theta}}.$$

XVII. *On the Thermal Behaviour of Liquids.*
By Prof. William Ramsay *and* Prof. Sydney Young.

To the Editors of the Philosophical Magazine.

Gentlemen,

DURING recent years several papers on the thermal properties of gases and liquids, which contain what we believe to be incorrect conclusions, have been published ; and in the interest of accurate knowledge we feel bound to make some comments on them, and to point out in what respects they are erroneous.

We shall first consider certain observations on the critical point.

Battelli (*Atti del R. Istituto Veneto di Scienze*, iv. serie vii. 1892–93 ; also a pamphlet published by Antonelli, Venice) comes to the following conclusions regarding the critical point:—

" 1. The critical temperature is that at which the cohesion of the liquid particles is so diminished that they no longer remain together, but expand throughout the containing vessel.

" 2. Above the critical temperature the liquid particles continue to vaporize, *i. e.* to separate into molecules of saturated vapour, as the temperature rises.

" 3. Retaining for the term ' critical point' the signification which it has in the isothermal diagram, the determination of the critical point (temperature ?) by means of the optical method is not generally exact ; because the disappearance of the meniscus takes place at a temperature higher than the critical temperature, and striæ (*intorbimento*) appear at a temperature the lower, the greater the amount of liquid contained in the experimental tube."

Again, in Wiedemann's *Annalen*, vol. l. p. 531, Galitzine states that the critical temperature, determined by heating the liquid and allowing it to cool until a meniscus is just visible, is lower than the true critical temperature. He also makes the remarkable assertion that at temperatures considerably higher than the critical temperature the substance at constant pressure may have different densities, varying as much as 25 per cent., *owing to the formation of liquid complexes* ! A short account of these conclusions is to be found in ' Nature,' November 23, 1893, and in this Journal, Dec. 1893, p. 552.

Zambiasi and de Heen also state that the temperature at which mist and striæ appear when the substance is cooled is lower than the true critical temperature, but in other respects

the results obtained by these two observers are contradictory. Zambiasi found that the temperature at which the meniscus disappears on heating is identical with that at which mist and striæ form on cooling; and that both temperatures are *lowered* by increasing the quantity of the liquid relatively to the vapour. De Heen, on the contrary, found that the temperature at which the meniscus disappears is *raised* on increasing the relative quantity of liquid; while Galitzine found the temperature at which the meniscus disappears to be higher than the temperature at which it appears, but both of them *practically independent* of the relative quantity of liquid.

Again, the critical temperatures of the esters given by de Heen differ enormously from those observed by Nadejdine and by one of us; that of methyl acetate differs by no less than 46°!

There can be little doubt that in most, if not in all of such experiments, the arrangements employed to maintain constant high temperatures must have been sadly defective. Battelli made use of fractions of petroleum-oil, boiling at intervals of temperature of 10°. This plan was tried by one of us as long ago as 1879, and subsequently rejected as entirely unsatisfactory. The heating arrangement employed by Galitzine would be satisfactory if the sample of naphthalene used as a jacket were pure. This method is a modification of that which we have constantly employed, and frequently recommended, during the last ten years; yet it is strange that while Galitzine refers to an early paper by one of us containing conclusions which have been acknowledged as erroneous in subsequent papers, he makes no reference to our later work, of which he appears to be ignorant. Moreover he relies on de Heen's work, which is very inaccurate. Precisely such conclusions as appear in these papers were given by one of us in the paper referred to (Proc. Roy. Soc. 1880, xxx. p. 323, and xxxi. p. 194), in which similar arguments were adduced in favour of liquid molecules, and of the non-identity of the liquid and gaseous states at and above the critical point. The author of that paper again takes this opportunity to say that he no longer believes in the conclusions; and he would regret the publication of that paper were it not for the hope that it may serve as a beacon to warn others, beginning to experiment on the subject, from the numerous rocks and shoals with which it is beset.

Since that paper was published we have been engaged on many pieces of joint work, and the critical constants of ether and of the alcohols have been determined with great care; the constants for no less than 18 other liquids have also been

determined by one of us. Our observations have led us to the following conclusions :—

1. If temperature and volume be kept quite constant, striæ are never seen, but only a blue, misty appearance.

2. It is absolutely essential that the whole of the substance should be equally heated, and this result cannot be attained if the vapour of an impure liquid be employed as a jacket.

3. It is equally essential that the liquid examined should be perfectly pure and free from air ; these precautions are especially important in the determinations of volumes near the critical point, since the smallest alteration in temperature or pressure produces a great alteration in volume ; and to this fact the erroneous conclusions referred to are in all probability to be attributed.

In certain cases, as for example with alcohols and acids, there may be molecular complexes at the critical point ; but we have no doubt whatever that the substance is physically homogeneous, as much so indeed as a thorough mixture of oxygen and hydrogen gases is ; and that the only difference in density in different regions is that due to the weight of the substance itself compressing the lower regions to a slightly different density than that of the upper regions, just as the density of the atmosphere at the level of the sea is greater than that on a mountain (see Gouy, *Compt. Rend.* 1892, p. 720).

These considerations are sufficient, we think, to explain the erroneous conclusions of the authors referred to.

It is necessary next to draw attention to an incorrect observation of Battelli, regarding the vapour-pressures of liquids and in particular of alcohol (*Memorie della Reale Accademia delle Scienze di Torino*, serie ii. tom. xliv. p. 11). He there states that he notices with alcohol what he has previously noticed with other liquids, that the vapour-pressure at a given temperature depends on the relative volumes of liquid and gas, increasing as the volume of liquid increases and gas diminishes, *i. e.* with decrease of volume. This observation is absolutely opposed to our experience, and implies one of two causes,—either that his sample of alcohol contained some other liquid, or that it contained some permanent gas. His data do not allow us to decide to which of these causes his results are to be attributed. It is also to be noted that the vapour-pressures which he records are in every case somewhat higher than those observed by Regnault and by ourselves.

Such work as that referred to requires the utmost care, especially in securing uniform known temperatures ; and it

is to be regretted that observations should be published, and conclusions drawn which are affected by errors easy to avoid by the use of pure vapours from liquids boiling under constant known pressures as a means of obtaining constant known temperatures. A little trouble taken at the beginning of a research in purifying the liquids employed as jackets is well-rewarded in the avoidance of erroneous observations during the progress of the research ; and inasmuch as many mathematical physicists are endeavouring to find some expression which will better fit facts than van der Waals' simple but approximate formula, it appears a pity that untrustworthy observations should be offered as a groundwork for their analysis.

<div style="text-align: right">

William Ramsay.
Sydney Young.

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XVIII. *Thermoelectric Diagram for some Pure Metals. By* W. Huey Steele, *M.A., Melbourne*[*].

SINCE 1873, so far as I am aware, no work on this subject has been published. In that year Professor Tait, in the Transactions of the Royal Society of Edinburgh, published " A First Approximation to a Thermoelectric Diagram," and stated that it was only an approximation and that other results would follow. The results in the paper above have since been accepted as the most reliable. In his paper he gives very little experimental detail, such as the method of observation, sensitiveness of galvanometer, &c., and the greater part of the paper is taken up with the behaviour of the iron line. In making some thermoelectric observations I had reason to suspect that his diagram was not quite right, and further measurements showed that the copper line was far from its right position. I determined therefore to construct a diagram for as many pure metals as I was able to obtain.

Whatever method of observation is adopted, one essential in thermoelectric observation is an exceedingly delicate galvanometer, that one being the best which indicates the least electromotive force applied to its terminals, not the one indicating the least current. Of the various sensitive galvanometers at my command, the best was a one-coil, low-resistance (about half an ohm), astatic instrument made by Elliot Bros. The needles, about 45 millim. in length, were

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* Communicated by the Author.

magnetized to saturation by flashing through a very great number of turns of fine wire round the needles as heavy a current as the wire would carry. They were then suspended, and the stronger gently stroked with a weak magnet till the desired sensibility was obtained. The system was quite stable in the earth's field, and the time of swing was about 10 seconds. The mirror was concave, with a focal length of 8 inches. A half-millimetre scale ruled on glass was placed about 60 inches from the mirror, between it and a well-lighted frosted window. The image of this scale was very sharply defined and permitted magnification by an eyepiece magnifying 10 diameters, the lines still being sharp and clear, and tenths of a division could be estimated. An electromotive force of ten absolute units produced a deflexion of one scale-division, and one absolute unit might be detected. A Thomson galvanometer of 10,000 ohms to be equally sensitive would have to indicate 10^{-12} amperes.

The method of observation may be learned from the accompanying diagram. E is a Clark cell joined in series with an
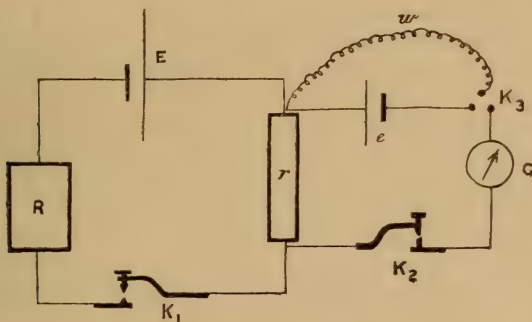
adjustable high resistance R, a known low resistance r, and a key K_1; as a shunt on r there is the thermal junction e, the galvanometer G, and a key K_2. A copper wire w, of the same resistance as the junction, is put across its ends in such a way that by means of the three-way key K_3 either this wire or the junction may be put into the gavanometer circuit. In making an observation w is put into the circuit, K_2 closed, and the deflexion, if any, observed. This comes from the unequally heated junctions forming the circuit; and so great was the sensitiveness of the galvanometer that even when there was nothing but copper and brass in circuit, and it had not been interfered with for some hours (the first thing in the morning

for example), a deflexion of a scale-division or two was always observed on closing K_2. This deflexion generally increased while observation was going on, chiefly from Peltier effects in r. This deflexion having been mentally noted, w was thrown out and e put in, K_1 and K_2 closed, and R adjusted till the deflexion was the same as that observed previously. Then e/E is equal to $r/(\mathrm{R}+r+\mathrm{E}_b)$, E_b being the internal resistance of E. I used the Clark cell, as it had been recommended by Prof. Threlfall (Phil. Mag. 1889, vol. xxviii.) as a good source of small constant currents. I made three according to Lord Rayleigh's instructions, and on testing them found that they gave consistent results when closed through resistances of not less than 6000, 5000, and 4000 ohms respectively. That is, the values of the internal resistance from any two observations with resistances higher than those mentioned were consistent, but began to vary when the cells were closed through less resistances. But after being closed through lower resistances, they quickly recovered on being left on open circuit. The resistances of the cells were 265, 43, and 50 ohms. In my observations I never used more than two thirds of the current that I might have as determined above, and when I wished to have a greater current (as was necessary in working with antimony) I put the three cells in parallel and closed through 3800 ohms.

When copper was one of the metals forming the pair under examination, the junctions of the copper with the two ends of the other metal, generally a wire, were immersed in beakers of oil, the junction formed by twisting the wires together being wrapped round the bulbs of the thermometers. When copper was not one of the pair, then the one junction was in a beaker of hot oil as before, and the two junctions of copper with the two other metals were kept in the same beaker of oil, insulation being of course attended to. By observing the temperatures of the hot and cold junctions on each occasion, it was not necessary to take any precautions to keep the cold junction at a constant temperature, as the correction to be applied was determined from each set of observations.

I did not go higher than 100° C. in observing, as I had shown (Proc. Roy. Soc. Victoria, 1893) that at high temperatures the ordinary thermoelectric formulæ fail, and occasionally I noticed irregularities coming in even at 100° C. In the paper quoted I have described some months' experiments in heating single conductors, in which I found that at the temperature of 1000° C. an irregular, arbitrary sort of an electromotive force may be obtained. This is sometimes

enormously high (as thermoelectric forces go), as in the case of half a dozen different metals I observed ·3 volt, about the same as that given by a junction of bismuth and antimony at that temperature, did the ordinary formulæ hold so far. At lower temperatures these irregular effects are not so great, being more than proportionately smaller, but still on several occasions I found them distinctly marked even as low as 200° C.

In any series of observations the relation between the observed values of the temperature T and E.M.F. *e* is of the form $e = a(T - T_0) + b(T - T_0)^2$, where T_0 is the temperature of the cold junction and *a* and *b* are constants to be determined, *b* being positive or negative, according as the lines of the two metals being examined intersect below or above T_0. In each, *a* and *b* were determined by the method of least squares. *e* having been calculated again in each case from the values of *a* and *b* thus obtained and the observed values of T, the means of the differences between the values of *e* thus calculated and those observed are given below in each case as the mean error in absolute units. To compare the error in different cases, I have also expressed it as the mean error in temperature. It will be noticed that frequently the discrepancies between different sets of observations on one junction are enormously greater than the mean error in one set, in spite of the fact that, as far as one could tell, they were in exactly the same condition in each case and were not even touched between the experiments. In view of the experiments referred to above and these discrepancies, one is led to the suspicion that the thermoelectric constants are not really constant, but that they vary in a given specimen in a manner which, if not arbitrary, yet arises from changes in condition which are inappreciable. I usually made three sets of observations on any pair of metals I examined, but with copper and lead I made more,—first to find out if the constants tended to become more constant, or, if not, to see if they varied in any regular manner ; and, secondly, because I had taken copper as a base-line for some metals which lay close to it, and it was therefore necessary to determine its position with more than usual accuracy. The following are the thermoelectric heights observed ; the metal with the higher line being in each case put first :—

	Relative height.	Mean error.		E.M.F. 0° to 100°.
Cadmium—Copper	$-4{\cdot}56 + 2{\cdot}756\ t$	27	$\overset{\circ}{\cdot}7$	13320
	$31{\cdot}32 + 2{\cdot}318\ t$	80	1·1	14720
	$-{\cdot}4\ \ +2{\cdot}930\ t$	20	·4	14670
Copper—Silver	$24{\cdot}8\ +\ {\cdot}090\ t$	34	1·3	2930
	$26{\cdot}7\ +\ {\cdot}052\ t$	71	2·6	2930
	$26{\cdot}5\ +\ {\cdot}062\ t$	50	1·9	2960
Copper—Gold	$20{\cdot}5\ -\ {\cdot}062\ t$	20	1·0	1740
	$24{\cdot}5\ -\ {\cdot}128\ t$	20	1·0	1810
	$22{\cdot}0\ -\ {\cdot}073\ t$	18	·9	1840
Antimony—Copper	$3330 + 18{\cdot}4\ t$	1400	·4	425000
	$3450 + 16{\cdot}6\ t$	......		428000
	$3890 + \ 8{\cdot}5\ t$	1670	·4	431000
Copper—Lead	$242 + 1{\cdot}84\ t$	91	·3	33400
	$272 + \ {\cdot}75\ t$	117	·4	30900
	$278 + 1{\cdot}29\ t$	108	·3	34200
	$279 + 1{\cdot}22\ t$	47	·2	34000
	$282 + 1{\cdot}13\ t$	63	·2	33800
	$287 + \ {\cdot}99\ t$	29	·1	33700
	$285 + 1{\cdot}11\ t$	40	·1	34100
	$282 + 1{\cdot}15\ t$	67	·2	33900
	$275 + 1{\cdot}34\ t$	103	·3	34200
	$267 + 1{\cdot}53\ t$	149	·5	34300
	$276 + 1{\cdot}25\ t$	52	·2	33800
	$283 + 1{\cdot}09\ t$	51	·2	33700
Copper—Tin	$287 + 1{\cdot}12\ t$	130	·4	34300
	$284 + \ {\cdot}94\ t$	140	·5	33100
	$296 + \ {\cdot}76\ t$	65	·2	33400
Lead—Tin	$11{\cdot}7 - {\cdot}065\ t$	17	1·6	850
	$8{\cdot}6 - {\cdot}003\ t$	16	2·0	850
	$10{\cdot}6 - {\cdot}025\ t$	6	·6	940
	$13{\cdot}6 - {\cdot}065\ t$	13	1·0	1040
Copper—Zinc	$203 - {\cdot}778\ t$	140	·7	16400
	$177 - {\cdot}196\ t$	35	·2	16700
	$185 - {\cdot}496\ t$	45	·3	16000
Zinc—Lead	$79{\cdot}3 + 2{\cdot}04\ t$	97	·9	18100
	$81{\cdot}2 + 1{\cdot}94\ t$	105	1·0	17800
	$70{\cdot}3 + 2{\cdot}11\ t$	96	·9	17500
	$73{\cdot}3 + 2{\cdot}06\ t$	71	·7	17600
Lead—Aluminium	$54{\cdot}8 - {\cdot}23\ t$	37	·7	4330
	$50{\cdot}9 - {\cdot}18\ t$	20	·4	4190
	$52{\cdot}3 - {\cdot}22\ t$	37	·7	4130
Thallium—Lead	$216 - {\cdot}79\ t$			

The column headed " mean error " shows the mean error of each set of observations, expressed in absolute units of E.M.F., and also in fractions of a degree. The last column is the calculated E.M.F. of a pair one of whose junctions is at 0° C., the other at 100° C. The discrepancies between the values determined from different sets of observations are very much greater than the mean error of a single set, which appears to indicate, as already mentioned, that the thermo-electric " constants " are not absolutely constant. In determining these constants, it is an open question whether they should be found from a short range of low temperatures, or whether a long range of temperatures should be observed. In the former case the most accurate observations can be taken, and are practically uninfluenced by the irregular effects mentioned above ; but in this case the Thomson effect comes in as a quantity of a much smaller order of magnitude than the absolute height. If the range of temperature be greater, the Thomson effect is a much more important quantity, and can consequently be determined more accurately. In this case, however, the accuracy of the observations is very seriously interfered with by the irregularity of the effect referred to above. Different ranges of temperature with different junctions might be advisable, but I considered that a range of 85° or 90° would give sufficiently accurate results. I was disappointed in some of them, *e. g.* antimony and cadmium, but in these the mean result is probably not very far from the truth, especially in calculating electromotive forces ; the error in the constants considered apart from one another is of course greater. In writing down the thermoelectric height of each relatively to lead, some metals will have two values ; that is, in cases of three metals where the three pairs were examined separately, as for instance in lead, copper, and zinc, the height of the zinc line might be taken as the observed height above lead, or the sum (or difference) of the lead-copper and copper-zinc heights. In this case, where the zinc line lies between the copper and the lead lines, the former of the two values will be the more accurate, and in estimating the position I have given the two values weight in the ratio of three to one. In the case of tin, which lies very close to lead compared with copper, I have taken the directly observed height as the true one, as the other is the difference of two large and nearly equal quantities—a very inaccurate method of observing the value. The following table is the result of all the observations, which is also shown graphically on the diagram with the exception of the antimony line :—

Aluminium	.	.	.	.	$-52\cdot7 +$	$\cdot21\,t$
Tin	.	.	.	.	$-11\cdot1 +$	$\cdot04\,t$
Lead	.	.	.	.	0	
Zinc	.	.	.	.	$80 +$	$1\cdot95\,t$
Thallium	.	.	.	.	$214 -$	$\cdot77\,t$
Silver	.	.	.	.	$250 +$	$1\cdot15\,t$
Gold	.	.	.	.	$254 +$	$1\cdot31\,t$
Copper	.	.	.	.	$276 +$	$1\cdot22\,t$
Cadmium	.	.	.	.	$285 +$	$3\cdot89\,t$
Antimony	.	.	.	.	$3558 +$	$14\cdot5\,t$
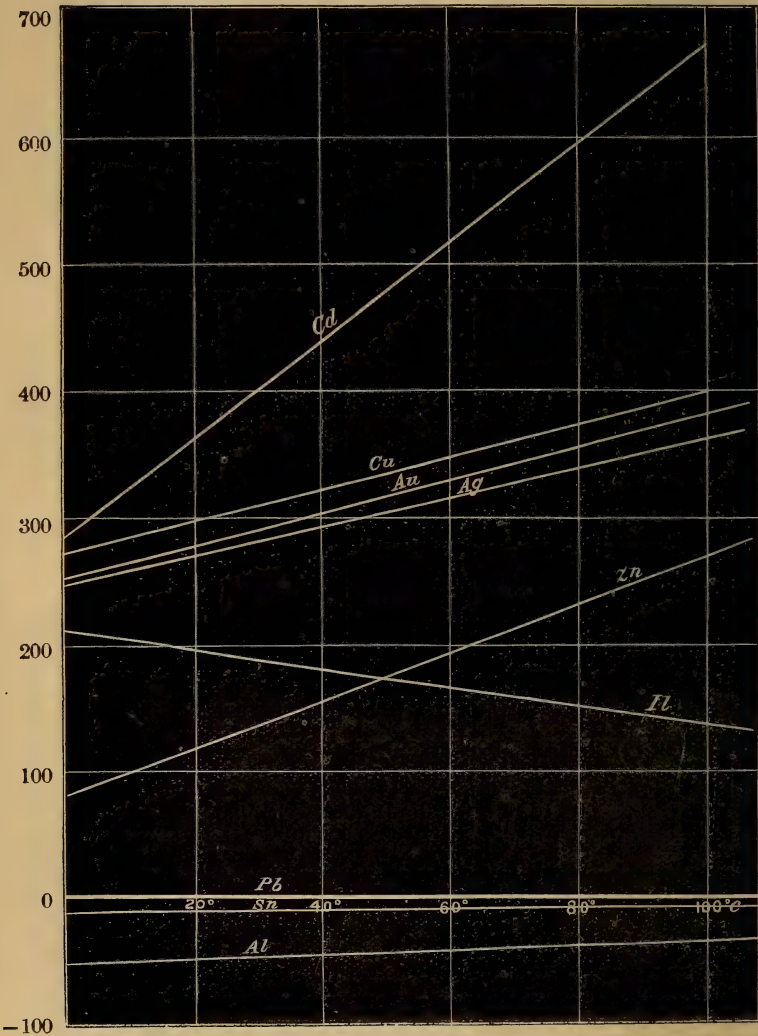
Metals Used.

Lead.—This was very pure, and was specially prepared for me by the method of Stas, by Mr. N. T. M. Wilsmore, M.Sc., F.C.S. Lead acetate was dissolved in water and digested for a week with sheet lead. The solution was filtered into hot dilute sulphuric acid, and the precipitated sulphate treated with water, dilute sulphuric acid, and again with water till perfectly free from acid. The sulphate was then stirred for some days in a beaker with solution of large excess of ammonium sesquicarbonate and ammonia, and washed till free from soluble ammonium sulphate. This treatment was repeated till the lead sulphate was nearly all converted into carbonate. A little of this was converted into monoxide by heating in a platinum dish, and the remainder nearly dissolved in dilute nitric acid, and the oxide added little by little, thus precipitating any iron which might be present. The solution was again filtered and added to solution of excess of pure ammonium sesquicarbonate and stirred, thus forming pure lead carbonate. This was dried and reduced under potassium cyanide in an unglazed porcelain crucible, the contents of which were poured into a polished steel mould. The lead button was washed with water, alcohol, and ether, and immediately placed in a glass tube with a narrow tube sealed on to the end. This was alternately exhausted and filled with pure hydrogen about a dozen times, and finally exhausted with a Sprengel and hermetically sealed. The lead was again melted and run into the narrow tube, a compact rod being thus obtained, which was drawn through draw-plates down to a wire of the desired size. All the reagents used were as pure as could be obtained, and were tested for impurities, especially metallic impurities, and when necessary were repurified. Mr. Wilsmore considered that the lead was free from all other metals, and from impurities of all kinds except perhaps a trace of oxide formed during the washing in water.

Silver.—This was prepared by Mr. W. Percy Wilkinson, Government Analyst, and considered by him to be "fairly pure." Silver chloride was reduced with wood charcoal and pure sodium carbonate. The ingot was washed with boiling water slightly acidulated with hydrochloric acid, and finally scrubbed with clean sand. This was re-dissolved in pure nitric acid, largely diluted, precipitated with dilute hydrochloric acid, washed with water, boiled with nitric acid,

washed with water, dried, digested with pure, hot hydrochloric acid, washed with boiling water, and dried at 100° C. The chloride was then reduced with pure sodium carbonate and wood charcoal, the ingot being treated as before. It was hammered into a rod with a polished steel hammer, on a similar anvil, and drawn through steel and agate draw-plates and annealed.

Antimony.—This was also prepared by Mr. Wilkinson, being reduced by him from pure antimony oxide, and considered by him to be " very pure." I melted it and cast it into a long rod in an iron mould, and broke off the ends and soldered them on at right angles so as to dip into the oil baths, and also soldered copper wires on to the ends to form the junction. (This was the only case in which I used solder ; in all others I merely twisted the wires together.)

Gold.—This was an exceedingly pure specimen supplied by the Melbourne branch of the Royal Mint. The percentage of gold being 99·994 according to the most delicate tests that could be made at the Mint. The Mint has also supplied the Physical Laboratory with a specimen of purity 99·998, but I was content to use the inferior of the two. The wire was drawn through three holes of the draw-plate after the last annealing, and may therefore be considered hard-drawn.

Zinc.—The zinc I used was supplied in rods by Messrs. Baird and Tatlock as pure redistilled zinc for making Clark cells. I could not draw it, and fused several rods end to end and bent it into the required shape.

Thallium.—This was given me by Mr. Wilkinson, who obtained it from Schuchardt as pure. Professor Masson analyzed it for me and found it contained 97·9 per cent of thallium, 1·5 per cent. lead, and traces of arsenic and copper.

Cadmium was also Schuchardt's pure, given me by Mr. Wilkinson. It was in form of a thick rod, which I hammered into a finer one and drew it through steel draw-plates.

Tin.—From same source and treated in same way as cadmium.

Copper.—" Pure Swedish Copper," as sold in the city for gold-refining processes. I used it in the hard-drawn state.

Aluminium.—Commercial Neuchâtel aluminium.

XIX. *On Ridge-Lines and Lines connected with them.*
By J. McCowan, *M.A., D.Sc., University College, Dundee**.

THE topography of mountainous regions, districts of
upland and valley, was discussed by Cayley, in 1859,
in a paper " On Contour and Slope Lines " †, and again by
Maxwell, in 1870, in a paper " On Hills and Dales" ‡. So far
as contour- and slope-lines are immediately concerned the dis-
cussion may therefore be regarded as complete ; but I desire
to define and call attention to certain lines connected with
these which I shall discuss in some detail in the following
paper, and which are especially characteristic of the general
configuration of a region of mountain and valley. These
lines I have called ridge-lines, but they are not to be con-
founded with those to which Cayley gave that name. The
word "ridge" as he employs it seems in general usage to have
given place to the term " watershed," used in its stead by Max-
well ; so perhaps I may be permitted to transfer it to the
lines I wish to discuss, as being specially descriptive of them.
It may be noted that in general there will be a ridge, as I
define it very near to, and in some cases coincident with, the
particular line of slope to which Cayley gave the name.

§ 1. *Contour-Lines and Lines of Slope.*

Consider the configuration of a surface, of any form, rela-
tively to a plane fixed with respect to it. This plane will be
called the base and will be regarded as horizontal, so that
planes parallel and perpendicular to it may be described as
horizontal and vertical planes respectively. The surface may
be, for example, that of any portion of land, and the base the
sea-level, provided that the part considered is not so large as
to require the curvature of the earth's surface to be taken
into account.

The curves in which the surface is intersected by horizontal
planes are called contour-lines, or simply contours. Lines on
the surface which cut the contours orthogonally are called
lines of slope : the inclination at any point of a line of slope to
the base is therefore equal to the inclination to the base of the
tangent plane at the same point and is a measure of the slope
there. Points at a maximum or minimum height above the
base at which horizontal tangent planes touch the surface are

called summits and immits respectively : all lines of slope run
from summits to immits, and obviously cannot cross each other
at any intermediate point, though a line may branch at any
point where there is a horizontal tangent plane.   At summits
and immits the surface is synclastic and the contours are
reduced to points ; but a horizontal plane may touch the sur-
face at a point, called a col, where the surface is anticlastic,
and where consequently two branches of a contour-line will in
general intersect, the point of contact being a double point of
the curve of section.   Other varieties of contact need not be
specially noted here as their occurrence is very exceptional.   In
the case of a land surface the summits are the tops of the hills,
and the immits the bottoms of lakes or basins, while the cols
are such points as the heads of passes between hills or places
where streams flow out from lakes.   The two lines of slope
from a col to the two adjacent summits form together what is
called a watershed, and the line of slope from a col to an
immit is called a watercourse[*].

§ 2. *Definition of Ridge-Lines.*

The section of a surface by a plane parallel and very near
to the tangent plane at any point, or, as it is generally called,
the indicatrix for that point, is in general a conic.   The
directions of the axes of this conic, depending only on the
form of the surface and not at all on its relation to the base,
are independent of the directions of the slope- and contour-
lines, and therefore the surface in the immediate neighbour-
hood of any point is in general unsymmetrical about the line
of slope through the point.   There are, however, points on
the surface at which the directions of the principal axes of
the indicatrix coincide with the directions of the slope- and
contour-lines, and the locus of such points is a line which I
propose to call a ridge-line.   The ridge-line, then, is defined
by this property:—A surface, in the immediate neighbourhood
of any point on a ridge-line, is symmetrical about the line of
slope through that point.

The topographical significance of the line is to be noted.
The features of a hilly country which are, perhaps, most cha-
racteristic are the ridges and spurs of the hills and the glens
or valleys between them.   The general trend of these features
is given by the ridge-lines, each ridge-line being, so to speak,
the central or axial line, the line of (infinitesimal) symmetry
of a ridge or valley—the valleys may be regarded as negative

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[*] For more detailed treatment of the matters of this section reference
may be made to the papers of Cayley and Maxwell, *loc. cit. ante.*

or inverted ridges. The ridge-lines run down the bottoms of the glens or along the tops of the ridges and spurs of the hills, or again down the lines where the descent is most precipitous.

Many of the most interesting properties of the ridge-lines may be derived almost immediately from the definition. For instance, it may be noted that wherever a line of slope or contour is crossed by a ridge-line, the lines of slope or contour touch the lines of curvature of the surface, for the directions of principal curvature are given by the axes of the indicatrix. It is most convenient, however, to proceed at once to the equation to the ridge-lines from which all such properties almost immediately follow.

§ 3. *The Equation to the Ridge-Lines.*

Take the base as the plane $z = 0$, z being measured vertically upwards. Let ξ, η, ζ be the coordinates of a point on the surface near to the point x, y, z also on the surface. Suppose, for the present, the surface to be determined by the equation

$$z = f(x, y). \qquad \qquad (1)$$

Then, employing the usual notation for the partial differential coefficients of z, the surface may, by Taylor's Theorem, be represented in the immediate neighbourhood of the point x, y, z by

$$\zeta = z + p\xi + q\eta + \tfrac{1}{2}\{r\xi^2 + 2s\xi\eta + t\eta^2\} + \&c. \qquad (2)$$

The indicatrix for the point x, y, z, that is, the section of the surface by the plane, parallel and very near to the tangent plane,

$$\zeta - \zeta' = z + p\xi + q\eta, \qquad \qquad (3)$$

will therefore be determined by

$$2\zeta' = r\xi^2 + 2s\xi\eta + t\eta^2, \qquad \qquad (4)$$

which is the equation to the projection of the indicatrix on the base. It will be convenient in future to use the word " projection " simply, whenever a projection on the base is to be understood.

At any point on a ridge-line the line of slope touches a principal axis of the indicatrix : the projections of these lines therefore touch also ; and so, if ϕ be the angle the projection of that axis of the indicatrix which touches the line of slope makes with the axis of x,

$$p/\cos \phi = q/\sin \phi. \qquad \qquad (5)$$

The directions of the axis of the conic (4) are, however, given by

$$(\cos^2\phi - \sin^2\phi)s = \cos\phi \cdot \sin\phi \cdot (r-t) ; \quad . \quad . \quad (6)$$

and on eliminating ϕ by (5) this gives

$$(p^2 - q^2)s = pq(r-t) ; \quad . \quad . \quad . \quad . \quad (7)$$

which must hold at all points on a ridge-line, and is therefore the equation to its projection. Equation (7) may be regarded as that of a cylinder whose intersection with the surface, given by (1), is the ridge-line. It will, however, be convenient to regard parts of the general locus as separate ridge-lines ; and in general each of the branches which passes through a multiple point, such as a summit or immit (*v. infra*), will be spoken of as a separate ridge or ridge-line.

It may be remarked that if the surface is given by an equation such as (1) of the *n*th degree, the equation (7) to the projections of the ridge-lines is of degree $3n-4$.

It is interesting to note, and the fact constitutes a not unimportant claim of the ridge-lines to attention, that whereas in many cases lines of slope and contour-lines cannot be found at all, being determined by differential equations which are in general not integrable in finite terms, the ridge-lines can always be deduced directly from the equation to the surface by mere differentiation.

§ 4. *The Relation of the Summits, Immits, &c. to the Ridge-Lines.*

The equation (7) which determines the ridge-lines is satisfied by $p=0$, $q=0$, and therefore—as is also geometrically obvious—all points at which the tangent plane is horizontal, that is to say, all summits, immits, cols, &c. lie on the ridge-lines : a result in accordance with the popular notion of a ridge, namely, a line running along the summits of a range of hills.

At such points equation (2), which gives the form of the adjacent surface, reduces, on neglecting terms of the third degree, to

$$\zeta = z + \tfrac{1}{2}\{r\xi^2 + 2s\xi\eta + t\eta^2\} ; \quad . \quad . \quad . \quad (8)$$

and therefore by (7), the projections of the ridge-lines are given by

$$\{(r\xi + s\eta)^2 - (s\xi + t\eta)^2\}s = (r\xi + s\eta)(s\xi + t\eta)(r-t),$$

which reduces to

$$(rt - s^2)\{s(\xi^2 - \eta^2) - (r-t)\xi\eta\}, \quad . \quad . \quad . \quad (9)$$

the equation to a pair of orthogonal straight lines, the projections, as is obvious from (8) or comparison with (6), of the principal axes of the indicatrix.

Thus in general through every summit, immit, and col two ridge-lines pass, crossing each other orthogonally and touching the lines of curvature, and therefore also the lines of slope; for at summits and immits all the lines of slope touch one of the lines of curvature, except one, a limiting case, which touches the other line of curvature[*], and at a col there are only two slope-lines coinciding with the lines of curvature.

In the foregoing it is supposed that the point, summit, immit, or col is an ordinary point on the surface; but if $rt = s^2$, or $s = 0$ and $r = t$, or $r = s = t = 0$, in which cases the point is a parabolic point, umbilic, or point of no curvature respectively, the equation (9) will vanish identically, and terms of the third degree must be retained in (8). The equation corresponding to (9) will then be of the third degree, so that three ridge-lines will in general cross each other at such a point; but as two of these may be imaginary, there may be in special cases only one ridge-line through the point—for instance, where the surface is a conicoid and the summit one of its umbilics.

The case in which the summit or immit is an umbilic may be examined. In this case $s = 0$ and $r = t$; hence, retaining terms of the third degree in (2), the surface near the point is given by

$$\zeta = z + \tfrac{1}{2} r \{\xi^2 + \eta^2\} + \tfrac{1}{6}\{a\xi^3 + 3b\xi^2\eta + 3c\xi\eta + d\eta^3\}; \quad . \quad (10)$$

and, by (7), this gives

$$(b\xi + c\eta)(\xi^2 - \eta^2) = \{(a - c)\xi + (b - d)\eta\}\xi\eta,$$

or

$$b\xi^3 + (2c - a)\xi^2\eta - (2b - d)\xi\eta^2 - c\eta^3 = 0, \quad . \quad . \quad (11)$$

as the equation to the projection, for points near the summit or immit, of the three ridge-lines which cross at the umbilic. This is the same equation as that which gives the three lines of curvature at the umbilic, so that the ridge-lines and lines of curvature there coincide. At an umbilic there is obviously no special connexion between the ridge- and slope-lines, for the latter proceed in all directions from such a point.

Other exceptional cases need only be mentioned. At particular points on a surface the indicatrix may have any form: if at any such point the tangent plane is horizontal, there will obviously be as many ridge-lines and lines of curvature

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[*] Cayley, *l. c. ante.*

through it as apses in the indicatrix, these lines passing through the apses.

It must be observed that the points here considered, that is to say points at which the tangent plane is horizontal, are not the only multiple points on the ridge locus. The geometrical characteristic of the others will be considered later.

§ 5. *Properties of the Ridge-Lines.*

It has already (§ 2) been pointed out that at points on a ridge-line the lines of curvature touch the slope- and contour-lines; hence their projections touch also. The projections of the slope- and contour-lines cut orthogonally everywhere, but in general those of the lines of curvature do not: they can only do so when they touch the lines of slope and contour. Thus, for all points on a ridge-line, but nowhere else, the projections of the lines of curvature cut orthogonally; or, in other words, the projection of the ridge-line is the locus of the points of orthogonal intersection of the projections of the lines of curvature.

This is otherwise obvious analytically, for the differential equation to the projections of the lines of curvature is

$$\{(1+q^2)s - pqt\}dy^2 + \{(1+q^2)r - (1+p^2)t\}dxdy$$
$$+ \{pqr - (1+p^2)s\}dx^2 = 0, \quad . \quad . \quad (12)$$

and these cut orthogonally wherever (7) is satisfied, for it makes the sum of the coefficients of dx^2 and dy^2 vanish. It may also be noted that (7) is obtained at once from (12) by the substitution of p and q for dx and dy, that is by imposing the condition that lines of slope and lines of curvature are to touch.

By transformation of (7) other interesting properties of the ridge-lines may be made immediately obvious.

Thus it may be written

$$q\frac{d\sigma}{dx} - p\frac{d\sigma}{dy} = 0, \quad . \quad . \quad . \quad . \quad (13)$$

where

$$\tan^2\sigma = p^2 + q^2. \quad . \quad . \quad . \quad . \quad (14)$$

By (14) σ is the angle of slope, that is the inclination of a line of slope or tangent plane to the base, and (13) shows that at any point on a ridge-line this does not vary along a contour. Thus at all points on a ridge-line the contour-lines touch the lines of a constant slope or isoclinics. The same fact may be otherwise expressed by saying that for each contour-line the slope is a minimum or maximum wherever it is crossed by a ridge-line. In this sense a ridge-line might

be called a line of minimum or maximum slope, and might have been defined by this property had not the definition chosen appeared the more fundamental.

Again, (7) may be written

$$p\frac{d\theta}{dx} + q\frac{d\theta}{dy} = 0, \quad \cdots \quad (15)$$

where

$$\tan\theta = -p/q, \quad \cdots \quad (16)$$

and θ is therefore the inclination of the projection of the line of slope to the axis of y. Thus (15) shows that at points on a ridge-line the projections of the lines of slope have no curvature, or, in other words, the projection of the ridge-line passes through the points of inflexion of the projections of the lines of slope.

§ 6. *The Ridge-Lines as particular members of a Family of Lines.*

The equations (13) and (15) suggest at once another point of view from which the ridge-lines may be regarded, namely, as members of the family of curves whose parameter γ is determined by one of the equivalent equations

$$(p^2 - q^2)s - pq(r - t) = (p^2 + q^2)^{3/2}\gamma, \quad \cdots \quad (17)$$

$$\frac{d\sigma}{dC} = \gamma, \quad \cdots \quad (18)$$

$$\frac{d\theta}{dS} = \gamma, \quad \cdots \quad (19)$$

where dC and dS are elements of contour- and slope-line projections respectively. The parameter γ is by (19) the curvature of the projection of the line of slope at any point, or, by (18), it may be interpreted as the rate at which at any point the slope-line turns round the contour-line as an axis per unit distance of advance along the contour. In passing, the interesting theorem thus given may be noted, namely, that the rate of twist of a slope-line about a contour-line at any point on a surface is equal to the curvature of the projection of the slope-line at the same point.

The ridge-line is the curve for which the parameter γ is zero, a value which obviously reduces the equations (17), (18), and (19) to the forms (7), (13), and (15) respectively. The curves for the general case, $\gamma = constant$, have not much special interest, but the consideration of γ leads to a simple geometrical characterization of those multiple points on the ridge-lines which were left over in § 4.

The conditions for a multiple point on any of the curves $\gamma = constant$ are

$$\frac{d\gamma}{dx} = 0, \quad \frac{d\gamma}{dy} = 0, \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (20)$$

which are also the conditions for a maximum or minimum value of γ. Hence the points of the surface for which γ, or, say for clearness, the curvature of the projections of the lines of slope is a maximum or minimum, are multiple points of the particular curves on which they lie. In the case of the ridge-line, $\gamma = 0$, and for a multiple point this must be a maximum or minimum value of γ. Thus, while in general the curvature of the projection of a line of slope changes from positive to negative in crossing a ridge-line, so that the point of crossing is a point of inflexion, at a multiple point the curvature will not in general change sign, and therefore the point will not be a point of inflexion. Hence, finally, the ridge-lines branch in general at points whose projections are points of no curvature but not points of inflexion on the projections of the lines of slope which pass through them.

§ 7. *Definition of Outlines. Contact Theorems.*

The consideration of another class of lines connected with the surface leads to a further interesting interpretation of equations (15) and (16).

Imagine a cylinder whose generating lines are horizontal to envelop the surface. This cylinder touches the surface along a line, the locus of the points of contact of the generators and contours. This line may be called an outline, for it is the line which would appear to bound the surface when seen from an infinitely distant point on one of the generators. There is of course a whole family of such lines, as the generators of the cylindric envelope may have any direction parallel to the base. Outlines corresponding to points at a finite distance and in any direction might be considered, but the more restricted definition chosen is sufficient for the purpose at present in view.

If θ, the inclination to the axis of x, of the generators of enveloping cylinder, be taken as the parameter for the outlines, then (16) is the equation to their projections, for it may be written

$$\cos \theta \frac{dz}{dx} + \sin \theta \frac{dz}{dy} = 0, \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (21)$$

which shows that the generators touch the contours wherever it is satisfied. Thus it is to be noted that, as in the case of

the ridge-lines, the outlines may be derived directly from the equation to the surface by differentiation only.

This interpretation of θ, as an outline parameter, leads to a corresponding interpretation of (15), namely—a line of slope touches an outline wherever a ridge-line crosses it. This points to a simple method of tracing the ridge-lines on a model of any surface if the lines of slope (or lines of curvature) are already traced on it. It is only necessary to view the surface from a point at a considerable distance in the base plane, and then, turning the model slowly round, to mark the points where the slope-lines (or lines of curvature) touch the continuously changing outline. The ridge-lines on a mountain could not be traced in a corresponding fashion, by a person moving round it at a sufficient distance, for there would be no means of identifying either slope-lines or lines of curvature on its surface.

Two general theorems with respect to the contact of the various lines considered have now been proved :—

I. At every point on a ridge-line, the outline, line of slope, and one of the lines of curvature have a common tangent.

II. At every point on a ridge-line, the isoclinic or line of contant slope, the contour-line, and the other line of curvature have a common tangent.

It is an immediate inference from the first of these theorems that if any line has at once the characteristics of any two of the lines there named it must also have the characteristics of the other two, and it easily follows that such can only be the case when the line is that of a section of the surface by a vertical plane. For example, suppose an outline to be a line of slope : it is therefore by I. a ridge-line, and therefore, again by I., a line of curvature. Further, since it is an outline p/q is constant, therefore, since it is also a line of slope, dy/dx is constant for the projection of the latter, which is thus a straight line, and the line itself is the section of the surface by a vertical plane through this.

Again, it follows in similar fashion from the second of these theorems that if a line has the characteristics of any two of the lines there named it must have also those of the other two, and in this case, being a contour-line, it is a section of the surface by a horizontal plane.

An obvious illustration of these results is afforded by surfaces having a plane of symmetry : if the plane is vertical the section by it is evidently a ridge-line, an outline, a line of slope, and a line of curvature ; but if the plane is horizontal the section is a ridge-line, a line of constant slope, a contour-line, and line of curvature.

§ 8. *General Considerations.*

Certain general inferences from equation (7) deserve notice. If $F(z)$ be substituted in it for z, it is only altered by the introduction of a factor (the cube of $F'(z)$). Thus if two surfaces have the same lines for the projection of their contours, the projections of their ridge-lines will also be the same, except that certain contour-lines (given by $F'(z) = 0$) may be ridge-lines for one of the surfaces only, ridge-lines all along which the surface touches horizontal tangent planes.

Again, a surface may have no definite ridge-lines, or, in other words, all points on the surface may satisfy (7) : in fact (7) may be regarded as the partial differential equation of such surfaces. In the form (13) the solution of this equation is obvious : thus, surfaces whose slope at any point depends only on the height of the point above the base have no definite ridge-lines, or, as it may be perhaps better put, every line of slope and every contour-line on such a surface is a ridge-line. Surfaces of revolution obviously belong to this class.

The conditions that a point on a surface may be an umbilic are

$$\frac{r}{1+p^2} = \frac{s}{pq} = \frac{t}{1+q^2}, \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (22)$$

for these make dy/dx indeterminate in (12). These ratios make (7) vanish identically : hence all the umbilics of any surface lie on ridge-lines. This is otherwise evident from the consideration that in the neighbourhood of an umbilic the lines of curvature have all directions. Again, (7) is identically satisfied at points where $r = s = t = 0$; that is to say, at points where the surface has no curvature. All such points therefore lie on the ridge-lines.

Again, it is geometrically obvious—or may be proved as below—that all singular points at which there is a tangent cone lie on ridge-lines. The three classes of points here shown to lie on the ridge-lines are peculiar to the surface : they have no relation to the base. This leads to the interesting result that while in general the ridge-lines on a surface will continuously vary when it is moved relatively to its base, these points will be fixed points through which they will continue to pass.

As the equation to a surface is in general most simply expressed in the form

$$\phi(x, y, z) = c, \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (23)$$

it is desirable before concluding to give the corresponding equation determining the ridge-lines. Still taking $z = 0$ as

the equation to the base, the ridge-lines will be determined by the intersection of the surface (23) and the surface whose equation is

$$\frac{d\phi}{dx}\frac{d\phi}{dy}\frac{d\phi}{dz}\left\{\frac{d^2\phi}{dx^2}-\frac{d^2\phi}{dy^2}\right\}-\frac{d\phi}{dz}\left\{\frac{d\phi^2}{dx^2}-\frac{d\phi^2}{dy^2}\right\}\frac{d^2\phi}{dx\,dy}$$

$$+\left\{\frac{d\phi^2}{dx^2}+\frac{d\phi^2}{dy^2}\right\}\left\{\frac{d\phi}{dx}\frac{d^2\phi}{dy\,dz}-\frac{d\phi}{dy}\frac{d^2\phi}{dx\,dz}\right\}=0. \quad . \quad (24)$$

The proof need not be given as it may be very easily supplied. It may be remarked that this is satisfied wherever

$$\frac{d\phi}{dx}=\frac{d\phi}{dy}=\frac{d\phi}{dz}=0, \quad . \quad . \quad . \quad . \quad (25)$$

so that all conical points lie on the ridge-lines, a result which is, however, obvious geometrically. If (23) is rational and integral and of the degree n, (24) will be of the degree $4n-5$, and therefore the ridge locus will be a curve of degree $4n^2-5n$.

XX. *Notices respecting New Books.*

A Treatise on the Mathematical Theory of Elasticity (*in two Volumes*). *By* A. E. H. LOVE, *M.A., Fellow and Lecturer of St. John's College, Cambridge.* Cambridge : at the University Press, 1893.

SOME apology would seem becoming for a delay of six months in noticing the first volume of this important contribution to our higher text-books in Mathematical Physics, were it not that there is always an advantage in considering at once the complete work. It speaks much for Mr. Love's devotion to the task he set himself, that the second volume has appeared so soon after the first—when a longer delay might well have been excused, or even expected.

The author informs us in the preface to vol. i. how this treatise originated in a suggestion of Mr. R. R. Webb that they should jointly prepare a work on Elasticity, but Mr. Webb's important avocations having prevented his cooperating, Mr. Love has had to take on himself the whole of the work—and it must have proved no light one. Following the excellent precedent of recent continental writers the author commences with an Introductory Historical Sketch of pp. 34, founded, of course, on the late Dr. Todhunter's History as edited and continued by Prof. K. Pearson. Herein the course of the Mathematical Theories of Elasticity is briefly traced from Hooke's enunciation of his famous law ' ut tensio sic vis ' in 1676 to those modern developments which Navier and Cauchy originated.

A good deal of space in this, as in other recent works on special branches of Mathematical Physics, is taken up—perhaps necessarily,

to make the treatise sufficient in itself—with such subjects as would be treated of once for all in a systematic work on the Principles of Natural Philosophy like Thomson and Tait's, to which preliminaries Mr. Love's first five chapters are devoted.

In Chapter vi. the treatment of concrete problems is commenced with the "Equilibrium of Beams," in solving which St. Venant and Clebsch are, of course, mainly followed. The analogy between the problem of the resistance of a cylindrical beam to flexure and the hydrodynamic question of the motion of frictionless liquid in a rotating cylindrical vessel is explained. There follow the "Torsion and Flexure Problems," very fully and clearly worked out in the practicable cases suitable for a text-book, with references to the sources for further recent developments. In a note at the end of vol. i. are some valuable remarks on Æolotropy; wherein the typographical slip of "luminated" for "laminated" may be pointed out, into which perhaps the printer was led by the occurrence of "luminiferous" lower down.

Chapter vii. is devoted to an exposition of "Curvilinear Coordinates," first introduced by Lamé in the *C. R.* for 1838. The method Mr. Love adopts is one founded on Mr. Webb's as given in his very able paper "Stress and Strain in Cylindrical and Polar Coordinates," *Messenger,* vol. xi. Some examples in illustration follow.

"General Solutions" occupy Chapters viii. and ix., wherein Betti, Cerruti, and Boussinesq are mainly followed; the solid strained, the dilatation and small motions in which are sought, being of no special form.

Chapter x. is occupied with the most recent generalization of Lamé's problem of the displacements of an elastic spherical shell; viz. a gravitating sphere subject to surface-tractions. Some account of the application of these results to the case of the elastic tides of the solid earth as discussed by Lord Kelvin and Prof. Darwin conclude the chapter.

Prof. Lamb's solution of the problem of the vibrations of an elastic sphere and spherical shell (Proc. L. M. S. xxiii., xxiv.) forms the subject of Chapter xi., as a particular example of the general theory explained in Chapter viii.

The subject of the application of curvilinear coordinates is further illustrated in the concluding chapter of vol. i.; and the application of conjugate functions to problems of elastic equilibrium.

In the second volume of Mr. Love's treatise are considered "in greater detail the special problems that arise when some linear dimensions of a body are small in comparison with others." The bending of rods in one plane; of rods and wires, with twisting, in three dimensions and the general theory of the same, as treated by Kirchhoff in particular, form the matter of Chapters xiii., xiv., and xv.; the theory of the small vibrations of thin rods that of xvi. Chapter xvii., treating of Resilience to Impact and Voigt's and Hertz's theories of Impact—the former taking account of the motions set up in the surface-films, the latter of the compression

therein as gradually subsiding—separates Chapter xviii., on the general theory of wires naturally curved, from xiv. and xv., to which it would seem more appropriately a sequel.

In Chapter xix. the elementary and then the general theory of thin plates is entered on; to be continued later in the concluding chapter (xxiii.), treating of the important question of the stability of elastic rods, plates, and shells—the intermediate Chapters xxi., xxii., dealing with the general theory of thin elastic shells and applications of the same.

It will be apparent from the foregoing glance at the contents of this treatise how wide a field it covers; and it may be added that where his plan and limits compel the author to exclude further developments ample references are given to the memoirs wherein they are to be sought. Frequent among these are references to Lord Kelvin's Mathematical and Physical Papers, and to Lord Rayleigh's, Prof. Lamb's, and Mr. Basset's papers in the Proceedings of the London Mathematical Society; also to Mr. Chree's in the Transactions of the Cambridge Philosophical Society. References to the sections on the subject of the treatise in Thomson and Tait's 'Natural Philosophy' and to Prof Pearson's exposition of St. Venant's work occur frequently, it is needless to say. Nor is Mr. Love himself only a judicious and careful compiler from the work of predecessors and contemporaries; his own original contributions to the sum of knowledge gained for the subjects on which he writes being considerable. A " Note on Kirchhoff's theory of the Deformation of Elastic Plates " and an elaborate memoir of 52 pages (" really an attempt to construct a theory of the vibration of bells ") on the same problem appeared in the Transactions of the Cambridge Philosophical Society and the Royal Society, respectively, for 1888; and since that date his papers have appeared in the London Mathematical Society's Proceedings at frequent intervals; while the present treatise is marked by all the thoroughness, accuracy, and candid confronting of difficulties which have characterized those original essays. This is, in short, a learned and valuable addition to the available text-books on departments of the higher Applied Mathematics.

Annals of British Geology, 1892. *By* J. F. BLAKE, *M.A., F.G.S.* 8vo. Pages i–xliv and 1–310, with 100 Illustrations. Dulau & Co.: London, 1893.

THIS is a careful and useful digest of the books, papers, and maps, published during the year 1892, that relate to British Geology for the most part, and to some extent to the Geology of the Colonies and of foreign countries.

It is the third of a series, the first and second of which have been noticed in the 'Philosophical Magazine' of March 1892 and February 1893. " In this third volume," the author remarks, " further changes of method have been introduced with a view of meeting the expressed wishes and suggestions of subscribers. The

criticisms or other observations on the papers are entirely separated from the abstracts; the few notes that will be found amongst the latter being designed only to render the author's meaning clear, or to point out the bearing of the statements he makes, by comparison with the statements of others on the same point . . . . The real criticisms or discussions of the subjects are collected together in the form of an Introductory Review" (pp. i–xliv); and this is of considerable interest as an excellent *résumé* of the newest and most important facts and opinions in Geology, so far as last year is concerned. Under General Geology in this "Review" (the papers and books are enumerated, with their abstracts, pp. 1–32) are included—the Earth's density and the condition of the Earth's Interior (pp. i–ix), organic agencies and subterranean erosion (p. ix), earth-folds and the age of folds (pp. x & xi), oceanic deposits (p. xi), and some faults (p. xii). Under Stratigraphical Geology (for papers &c., see pp. 32–122) we have remarks on the Archæan, the Torridian, the Cambrian or Monian in Shropshire, Cambrian in North Wales, and the Olenellus-zone (pp. xi–xiv), Devonian, Culm-measures, Permian and Trias, and Bunter pebbles (pp. xiv–xvi), Lias, Jurassic, and Speeton Clay (pp. xvi–xix), the Bagshots, Glacial gravels and Boulder-clay, and Rubble-drift (pp. xix–xxi), Ice in the English Channel and date and causes of the Glacial Period (pp. xxi–xxiv), the boring at Dover, and evidences of depression derived from borings (pp. xxiv–xxvii).

Under Palæontology (papers &c., pp. 127–184)—Human Imple-. ments, fossil reptiles, fossil fishes, cephalopoda, gasteropoda, insects, trilobites, and foraminifera (pp. xxvii–xxxii). Under Palæobotany (papers &c., pp. 184–195)—the Devonian flora, Stigmaria, Carboniferous Equisetum, and plant-remains in igneous rocks (pp. xxxii–xxxiv).

Under Mineralogy and Petrology (papers &c., pp. 195–231)—the sequence of plutonic rocks, Dartmoor granite, quartz in basic rocks, age of crystalline schists, schists of the Lizard, of Malvern, and of Sark (pp. xxxiv–xxxix), rutile in clay-slate, and quartz-knobs and quartzite (pp. xl–xlii).

The papers and reports on Economics (minerals, coals, building-stones, and water-supply) are enumerated at pp. 231–247; maps and sections, p. xlii and pp. 247–257. Foreign geology, described and illustrated in Britain, is treated at pp. xlii–xliv; and under successive appropriate headings at pp. 259–301.

The numerous illustrations, comprising some diagrams and plans, some sections, and many figures of fossils, carefully reproduced from photographs, engravings, woodcuts, &c., by permission of Authors and Societies, are far more satisfactory than the plates of well-intended, but poor, outline figures in last year's volume. The favourable chance, however, of borrowing big photographs or cuts has tempted the author here and there to lavish some extra pages and even leaves on pretentious objects.

Great labour and expense have been spent on this work by its

enthusiastic author, whose scientific acumen, wide knowledge, and judicious treatment of the varied subjects of his compilation are certainly further proved by this volume. As yet, he informs us in the Preface, the enterprise has not been profitable; but he hopes that it will be successful by the co-operation of more and more Subscribers; and indeed we sincerely hope that this handy and valuable Annual will be worthily supported.

XXI. *Intelligence and Miscellaneous Articles.*

ON THE NATURE OF THE REFLEXION OF ELECTRICAL WAVES AT THE END OF A CONDUCTING WIRE. BY MM. KR. BIRKELAND AND E. SARASIN.

IN a communication of April 17, 1893, one of us attempted, starting from the theory of the motion of electromagnetic energy in space, to make a hypothesis on what takes place in the vicinity of the end of a metal wire along which electrical waves are passing.

We have examined the question together, exploring the electrical field about the end of the wire, with small resonators of 10 to 25 centim. in diameter, and although the point of view explained in the note in question has not been confirmed in all points by our results, they form none the less an interesting experimental contribution to the remarkable theories of Prof. Poynting.

The electrical waves were furnished by a small plate-exciter, the sparks of which, about 3 millim., passed in oil. Opposite one of these primary disks was a similar one from which proceeded a copper tube 1 centim. in diameter and 9 metres in length. This tube was supported on thin wooden rods 1·5 metre high.

The resonators were circular and fixed vertically with the spark uppermost; they had a double motion—they could be rotated about a vertical axis passing through the spark, and they could also be moved parallel to the conducting tube.

We arranged so that even in darkness we could mark the distance from the centre of our resonator to the end of the conducting wire, measured parallel to the wire, and also the angle which the plane of this formed with the wire.

The observations were made by means of a telescope mounted horizontally at a distance of a metre from the circle, which is necessary owing to the considerable disturbance produced by the body of the observer on the rapid oscillations.

Our researches were directed to two points principally: we first determined the four first nodes in seven different distances from the wire; the plane of the circle being always normal to this. These nodes are each determined by at least ten measurements; the numerical results thus obtained for the circle of 10 centim. are given in the subjoined table. The different distances of the resonator from the conducting wire are counted from the axis of this latter to the nearest point of the circle. The numbers in each column give the distance of each node to the normal at the end of the wire.

Distance of the resonator from the conducting wire.	cm. 2.	cm. 10.	cm. 20.	cm. 30.	cm. 40.	cm. 50.	cm. 60.
First node.................	16·0	15·4	9·5	7·7	1·8	−9·8	
Second „	56·4	56·3	54·2	51·5	47·3	44·8	37·7
Third „	96·5	95·7	95·2	93·5	90·5	88·9	87·5
Fourth „	135·0	135·8	135·1	134·6	130·8	129·7	130·5
First loop...:.............	40·4	40·9	44·7	43·8	45·5	54·6	
Second „	40·1	39·4	41·0	42·0	43·2	44·1	49·8
Third „	38·5	40·1	39·9	41·1	40·3	40·8	43·0

In fig. 1 we have represented by small dots the position *of the centre* of the resonator of 10 centim. in the 27 nodes given numerically above. The small circles on the same figure give the positions of the nodes due to a circle 25 centim. in diameter in four different distances from the conducting tube.

The impression which directly results from the distribution of all these nodes is that, if the first *shock* arrives at the resonator almost parallel to the conducting wire, the second must arrive there by a direct radiation proceeding from the neighbourhood of the end of the wire. In fact all the nodes are situated virtually as if the energy producing the second *shock* in the resonator travelled *quite close* to the wire until it arrived at the end, and thence moved directly on the circle. It must, however, be observed that this mode of viewing the reflexion does not justify the considerable recession of the first node when the resonator is close to the

Fig. 1.

conducting wire; a recession which, according to the experiments of Sarasin and De la Rive, is greater as the circle itself is greater. We believe, however, we have now well established that this recession is due to the geometrical form of the resonator; the electrical shocks, arriving along two rectilinear conductors, tend

each to charge the nearest point of the resonator, so that the first oscillation is produced between the diametrically opposite parts of the circle. As, however, the electricity tends to oscillate in all the amplitude of the circle, this takes then its normal period, and the nodes are arranged along the wire.

We have in the second place investigated how the plane of the resonator must be turned about its vertical axis in order that the total effect of the two "shocks" which excite the oscillation may be as great as possible.

These directions are indicated in fig. 1. They have for the most part been determined where the maxima should be according to the measurement of the nodes. Among other orientations figured are two which have been taken in the nodes (dotted lines). These directions of maximum effect pronounce strongly, it seems to us, for a direct radiation from the end of the wire.

Of the three series of observations made in the centre of the loops it follows that the perpendicular to the circle is almost along the bisectrix of the angle which the line going directly to the end of the wire forms with the parallel to the conducting wire. The two observations made in the nodes themselves show that to have the maximum effect the circle must be orientated so that the electrical undulations coming from the end of the wire arrive perpendicularly to its plane, and that the action of the second shock is by this fact annulled.

The results which we have enunciated enable us to give a certain development to the conception of the moving electrical tube devised by some English men of science. Assume that the electrical tube of the *direct wave*, which moves at each point at right angles to its

Fig. 2.
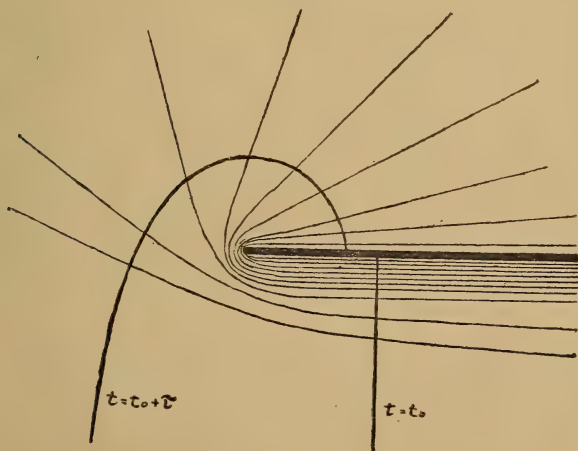
momentary direction, is almost rectilinear, and at right angles to the conducting wire: this will no longer be the case with the reflected wave.

Now measurements made by one of us of the interferences on the surface itself of the conducting wire show that in this case there is no appreciable recession of the first node, and that therefore the part of the electrical tube immediately near the conductor turns about the end of this almost instantly. But the distant parts of the tube cannot traverse simultaneously the same angular distance ; they remain behind and the electrical tube curves then almost like the tail of a comet about the end of the wire (fig. 2).

This would be the origin of this characteristic radiation proceeding from the end of the conductor, the existence of which we may admit. It would follow from this that as the elements of the tube continue to move at right angles to their direction for the time being, the energy escapes from the end of the wire and is lost in the surrounding space [*].—*Comptes Rendus,* Nov. 6, 1893.

DENSITIES IN THE EARTH'S CRUST.

To the Editors of the Philosophical Magazine and Journal.

GENTLEMEN,

Probably many of your readers will have read the Introductory Review in Mr. Blake's 'Annals of British Geology' for 1892, and will, like myself, have been surprised at the very direct manner in which he has impugned the accuracy of Mr. O. Fisher's conclusions regarding the comparative densities and thicknesses of those parts of the earth's crust which underlie oceans and continents respectively.

Mr. Blake undertakes to show that Mr. Fisher's method " is wholly fallacious." After stating the method referred to, he gives three reasons from which " it is easily seen that this method cannot lead to correct results." The manner in which these reasons are expressed does not make it clear to the ordinary reader that Mr. Blake has entirely upset Mr. Fisher's reasoning ; but when he narrows the issue to " the definite point where the fallacy comes in," the non-mathematical geologist must wish to know how far Mr. Blake's mathematics are correct.

I think that all who are interested in terrestrial physics must hope that Mr. Fisher will either admit or deny the value of Mr. Blake's criticism, and as he cannot reply in the 'Annals of British Geology,' perhaps he will favour your readers with a note on the subject, the issues being of considerable importance.

A. J. JUKES-BROWNE.

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[*] There should be an appreciable loss of energy on reflexion. We hoped to complete our research in this direction by measurements on the wire itself (*conf.* Birkeland, Wied. *Ann.* vol. xlvii. p. 583). For three wave-lengths $\lambda_1 = 6\,m$, $\lambda_2 = 2\cdot7\,m$, and $\lambda_3 = 1\cdot2\,m$, we found the reflected wave respectively 0·6, 0·45, and 0·35 of the direct wave. But we have devised another method of directly measuring the loss and we have not again found these values, so that we only give them under reserve, not having succeeded in explaining these contradictory results.

XXII. *The Luminosity of Gases.*
By Arthur Smithells, *B.Sc.*[*]

Part I.—*The Luminosity of Flames free from Solid
Particles* [†].

IN a brief note communicated to the Chemical Society in
1892 (Proc. Chem. Soc. no. 105) I described some
experiments on flame-coloration made with my flame-cone
separating apparatus, and in order to explain the results ob-
tained I adopted provisionally the view that flame-spectra in
some cases must be regarded as the direct effect of chemical
action.

Almost simultaneously E. Pringsheim read before the Akad.
d. Wissenschaften, Berlin, a paper on " Kirchhoff's Law and
the Radiation of Gases," which was subsequently printed
in Wied. *Ann.* xlv. p. 428, 1892. In this paper Pringsheim
records an elaborate series of experiments on the radiation and
absorption of sodium vapour, and arrives at the conclusion
that the spectrum of sodium salts in a flame and of sodium
vapour heated in neutral gases is due directly to chemical
action. In a subsequent paper [‡] Pringsheim has extended his
experiments to other substances and has obtained similar
results.

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[*] Communicated by the Author.
[†] A summary of this part of the paper was read before the Chemical
Section at the Nottingham meeting of the British Association, Sept. 19,
1893.
[‡] Wied. *Ann.* xlix. p. 347 (1893).

This unexpected confirmation of the conclusion suggested by my own experiments increased my belief in its probable correctness, and further evidence in its favour appeared from a consideration of well-known facts of spectrum analysis.

Having been requested to show the experiments at the British Association at Edinburgh in 1892, I brought the matter before Section A, where it roused an animated discussion. Widely different views were expressed. Professor von Helmholtz held the opinion that flame-coloration and the luminosity of gas-flames not containing solid carbon must be attributed to radiation consequent on chemical action ; on the other hand, Sir G. G. Stokes did not consider that there was any conclusive evidence in favour of this view.

Object of the Experiments.—The object of what follows in this paper is to ascertain how far the luminous radiation from gaseous flames (including " non-luminous " gas-flames and such flames coloured by metallic salts) may be ascribed to *incandescence*, and whether any other cause has to be sought for an explanation of the phenomena observed. By incandescence is meant the evolution of light as a direct consequence of the application of heat.

The currently accepted Doctrine.—When a small quantity of common salt or other salt of sodium is introduced into the flame of a Bunsen-burner a yellow flame is produced, which is ordinarily ascribed to the vapour of metallic sodium glowing in consequence of the high temperature of its surroundings. The green-blue flame due to copper chloride under the same circumstances is attributed to the incandescent vapour of copper chloride. With calcium chloride the red flame which is obtained is said to be due to the vapour of calcium chloride and of calcium oxide. These may be taken as typical cases.

The authority for these views dates back, as is well known, from the earliest days of spectrum analysis. One or two questions connected with them which are at once obvious to the chemist are as a rule passed over in silence. If it be asked, for instance, how does sodium vapour become free in the flame, what answer is to be given ? The usual answer, I believe, has been that the salt is *dissociated*, notwithstanding that we have no other evidence of the dissociability of sodium chloride at any attainable temperature[*]. Another explanation that I have seen, and that only once, is given by Mendeléeff in his ' Principles of Chemistry ' (vol. i. p. 563). He says that the NaCl is acted upon by steam in the flame to produce NaHO

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[*] Sir G. G. Stokes informs me that he has never entertained this view, but it has certainly been widely expressed.

and that this is subsequently reduced by the carbonaceous matter of the flame. Again, it may be asked how is it that copper chloride, which is known to lose its chlorine at quite moderate temperatures, can not only be vaporized but be made incandescent in a flame, and in a flame too which contains reducing gases?

The solution of the difficulties here presented is not so obvious that it should be withheld, yet I have been unable in searching the literature of spectrum analysis to find any discussion of these fundamental questions.

With regard to the luminosity of " non-luminous " gas-flames and the luminosity of gases in Geissler-tubes the difficulty has been to some extent grappled with, and as such flames are the media in which colorations are obtained it will be convenient to discuss them first.

Attempts to produce Luminosity in Gases by External Heating.—The consideration of the luminosity of flames free from solid matter, such as the flame of hydrogen or the ordinary Bunsen gas-flame, has been held to involve the question as to whether gases can be made luminous simply by increasing their temperature. The luminosity of gases through which the electric discharge is passed and of those in a flame may be directly due, it is alleged, in the first case to the electricity, and in the second to the chemical processes.

At the end of last century Wedgewood (Phil. Trans. 1792, p. 271) performed an experiment which proved that a current of air sufficiently hot to raise a strip of gold to bright redness possessed no luminosity.

In 1879 Hittorf (Wied. *Ann.* vii. pp. 587, 591, and *ibid.* xix. p. 73, 1883) found that on passing an electric current from a battery consisting of 1600 elements through air at a pressure above 15 millim. the platinum electrodes became white-hot, yet the air in their immediate neighbourhood showed no luminosity even when the platinum was melting. He found the same to be the case when pure iridium electrodes were employed. These when melting communicated no luminosity to nitrogen, hydrogen, or carbon monoxide. He concluded that the luminosity and line-spectra of gases could only be obtained at much higher temperatures developed by the momentary discharge of a condenser. He adds :—" The light of ordinary flames, which do not contain solid particles, is not determined by the temperature but by chemical processes and must be regarded as phosphorescence. For if these gases acquire the temperature of the flame, without being involved in the chemical process, they radiate no light perceptible to the eye. One can convince oneself of this by

hanging horizontally a narrow cylinder with open ends and made of the thinnest platinum-foil in the hottest part of the flame given by a Bunsen-burner with fully open air-holes. In order to keep the radiation of the hot metal from the eye one looks through a narrow tube laid in the direction of the axis of the platinum cylinder, and the experiment is performed in a dark room. The gas within the tube appears dark to the eye and different from that of the luminous flame. Gases give the same result when in tubes made white-hot by a coal-fire." Hittorf refers to the observations of Wedgewood (*vide supra*) and Melloni (Pogg. *Ann.* lxxv. p. 62, 1848) on the same subject.

In 1882 Werner von Siemens, unaware of the work just referred to, made experiments with a Siemens regenerative gas-furnace and found that oxygen, nitrogen, steam, and carbon dioxide possessed no luminosity at a temperature somewhat above 1500° C. In confirmation of this conclusion he points out that, when a flame is made hotter by increasing the air-supply or previously heating it, the visible flames become smaller although the products of combustion must be hotter. If the luminosity of flame were due to the simple glowing of the products of combustion, the visible flame should increase and not diminish in size under the conditions just described. The luminous region of flame is therefore conterminous with the region of chemical action and (he argues) is directly due to it. He adds :—" If we assume that the gas molecules are surrounded by a sheath of æther an alteration of these sheaths of æther must take place when two or more such molecules combine. The resultant movement of the æther particles must be compensated by vibrations which can form the origin of the flow of heat and light waves. In quite a similar way we can picture the light-effects which appear when an electric current is passed through gases."

The Internal Condition of Flame.

The experiments of Hittorf and Siemens may, I think, be held to establish two facts—(i.) That air, carbon monoxide, steam, and carbon dioxide emit no sensible light when at an average temperature of 1500° C. or perhaps 3000° C.; (ii.) That the luminous part of flame is conterminous with the region of chemical action. They do not establish, I think, a third and most important conclusion, namely, that the luminosity is due directly to chemical action and not to heat. Before such a conclusion can be justified we must be sure that the products of combustion in the flame do not exceed 1500° or 3000° C.

It is assumed by Hittorf and Siemens, and has also been

assumed by Pringsheim (*loc. cit.*), that we are justified in speaking of the temperature of a flame as the temperature indicated by thermometric instruments when they are introduced into the flame. This seems to me to be fundamentally erroneous. Such a recorded temperature is no doubt the effective temperature of the flame, but it is merely an average temperature.

Every chemical student knows that the thinner the platinum wire he uses the hotter it becomes when introduced into a Bunsen flame, and it matters not whether the measurements of temperature depend on the fusibility of metals or salts, on specific heat, expansion, thermoelectric junctions, or electrical resistance, they are all open to the obvious objection that they only give the mean temperature of a considerable region of the flame uncorrected for conduction losses. What are we to say of the temperature of a candle-flame which will not melt a small bead of common salt but which will melt a platinum wire if pure and of a certain fineness ?

We may best deal with the matter by considering an ideal flame. Let us suppose that we have hydrogen issuing from a vertical cylindrical tube into oxygen gas, and let us consider a horizontal slice of the gas one molecule thick moving upwards in the tube.

For the sake of simplicity we may neglect the molecular motion of the gas, and we will also suppose the gas to inflame spontaneously on meeting with the requisite oxygen. The slice of gas as it ascends the tube is retarded by friction at the edges and will issue with a conical form from the tube. Here it inflames and gives us a small conical flame. This flame would consist of a conical sheet of hydrogen, one molecule thick, combining with oxygen. If we are to measure the temperature at the locus of combination we must have a thermometric instrument small compared with the thickness of the sheet of combustion. If the instrument does not fulfil this condition, it will protrude into the unburnt gas within the cone and the cooling gases outside, and the temperature indicated will be the average of the whole region in which it is immersed.

It may be objected that this is only an ideal flame, and that the conical sheath of flame actually obtained when hydrogen burns in oxygen has a very sensible thickness. This is no doubt true ; but it must be at once pointed out that if the sheath of burning hydrogen has a sensible thickness, that is to say if the hydrogen is burning on the outside surface, the inside surface, and in the intervening thickness of the sheath, hydrogen must all the while be passing through the sheath

without undergoing combustion, in order that there may be some on the outer surface to maintain the combustion there taking place ; and oxygen must be passing through from the outside to maintain the combustion of the hydrogen on the inner surface. If, then, we can get a thermometric instrument small enough to be wholly immersed in the region of combustion, the temperature indicated will not be that of the steam just formed but the average temperature of the hydrogen, oxygen, and steam within the sheath.

From this I think it is plain that no thermometric instrument can possibly indicate the temperature of the product of combustion in a flame at the moment of its formation. The temperature of 1500° ascribed to the hottest part of a Bunsen flame is therefore not the temperature of the products of combustion, and experiments that show these products to be non-luminous at a temperature even of 3000° C. afford no proof that the luminosity of flame is due to some other cause than the mere high temperature of the products.

How, then, are we to ascertain the temperature of the products of combustion ? The only remaining method is to calculate it theoretically. This may be done if we make the assumption (which must be considered as doubtful in view of recent experiments) that the specific heat of gases does not alter greatly with increase of temperature.

In the production of 18 grammes of steam from 2 grammes of hydrogen and 16 grammes of oxygen there are evolved 57,560 calories. The specific heat of steam being ·4805 we have the rise of temperature :—

$$t_2 - t_1 = \frac{57560}{18 \times ·4805} = 6655°.$$

This temperature then (with the proviso as to the constancy of specific heat of steam) must be the temperature of the steam-molecules formed in a flame of hydrogen, assuming the whole heat liberated during the reaction to be stored in the newly-formed molecules. It is well known that steam begins to dissociate far below this temperature, but the question of dissociation only enters into our present consideration in this respect, that it forbids us to assume a hydrogen-flame as consisting of molecules all in the act of combining. Whatever the degree of dissociation there is plainly some combination taking place, and if the heat liberated is stored in the molecules formed their temperature must rise to the theoretical 6600°. Even the average thermometric temperature of a hydrogen-flame is above the temperature at which dissociation of steam begins, and there must be therefore a certain number of un-

combined hydrogen and oxygen molecules in the flame. Our theoretical temperature of flame is no more an indication of its average temperature than its average temperature is a measure of the temperature of the steam which it contains. A gas may in fact exhibit a certain average temperature in two ways—it may have been raised to the average temperature by external heating or by internal chemical combination. In both cases the velocity of the molecules shows the same average, but this average is very differently compounded in the two cases. In the first case it can be shown theoretically that the number of molecules having velocities four times the average is extremely small. In the second case (flames) we have a large number of molecules of intensely high temperature and a large number of low temperature. The average temperature is in this case compounded of two extremes, and there is every reason to anticipate a difference of physical qualities. This difference we might reasonably expect to manifest itself in the emission of light by the gas which contains the intensely-heated molecules.

Similar considerations apply to the temperature of carbonic acid produced in flames. The theoretical temperature for the combustion of carbonic oxide in oxygen is 7180° C.

As neither steam nor carbon dioxide has been raised by external heating to anything approaching the temperatures we have indicated as accruing to them theoretically in the act of formation, it is still possible that the luminosity of flames in which they are produced may be due to high temperature in the ordinary sense of the term. The remark of Siemens (*supra*) that flames become smaller on increasing or heating the air-supply does not affect the conclusion arrived at, for it is not claimed that the luminosity of the products of combustion is of appreciable duration. Admixture with more air produces a smaller region of combustion, for it spares the combustible gas the necessity of wandering outwards to find the necessary oxygen. There would be in consequence a greater number of hydrogen and oxygen molecules uniting within a given space, the flame would be brighter but not necessarily larger, and this is certainly the case.

It may be stated further, in relation to the luminosity of air, steam, and carbon dioxide, that having regard to their extremely small optical absorptive power it is not to be expected that they will show any great emissive power even when raised to very high temperatures. The degree of luminosity shown by a Bunsen gas-flame, assuming the products to have the temperature calculated theoretically, appears to be just about what we might expect from *à priori* considerations.

Incandescent Iodine Vapour.

Having discussed the above question with Sir G. G. Stokes, I tried, at his suggestion, the experiment of heating iodine vapour. This, being strongly absorptive at ordinary temperatures, might be expected to emit visible radiations at comparatively low temperatures.

The experiment was made by filling the bowl of a "churchwarden" tobacco-pipe with iodine and closing with a lute of plaster of Paris. The stem was laid along a Fletcher tube-furnace and strongly heated. The bowl of the pipe, which protruded from one end, was heated with the flame of a Bunsen-burner. The tip of the stem, which protruded about one inch from the other end, was shielded from stray light and viewed against a background of black velvet. When the stem was heated to such temperature as could be obtained with the unforced draught of air, the issuing stream of iodine vapour was not luminous; but when the furnace was fed with a blast of air and the temperature sufficient to soften the pipe, the iodine became luminous and the vapour presented the appearance of a pointed yellowish flame about an inch in length. A similar appearance was obtained when a glazed porcelain tube was substituted for the pipe-stem, so as to exclude all possibility of furnace-gases diffusing into the interior. My attention was subsequently drawn to the fact that the effect had been already described by Salet (Pogg. *Ann.* cxlvii. p. 319) and had been achieved in a simpler way.

The experiment may be best performed as follows:—A piece of hard glass tube about half inch diameter and five inches long and closed at one end is suspended horizontally by platinum wires from the ring of a retort-stand and heated along its whole length by the flame of a flat Bunsen-burner. This should be done in the dark, and the burner removed as soon as the glass is seen to glow. The tube is allowed to cool till it has just ceased to glow, and then a long piece of platinum-foil bent into a trough and filled with iodine is passed into the tube and the iodine tipped out. The tube is immediately filled with the glowing vapour of iodine. This can be made to glow still more brightly by a reapplication of the flame. How much of the luminosity is due to the iodine and how much to the hot glass may be seen at any moment by blowing out the iodine vapour by a puff of air. The effect is very marked, and there seems no room to doubt that the glowing is due to hot iodine vapour. The lowness of the temperature seems to forbid the suggestion that the glow may be due to combination of the iodine with

oxygen or to the dissociation and recombination of the atoms of the iodine molecule.

The result of this experiment is in conformity with the views already expressed as to the luminosity of flame and enables us to see that, whilst colourless gases like those forming the products of ordinary combustion are not likely to glow at the average temperature of a flame, they would at some higher temperature emit visible radiations.

The chief conclusions arrived at in this part of the paper are :—

1. That in speaking of the temperatures of gases regard must be paid to the mode of heating.

2. That external heating produces an average temperature compounded in a different way from the same temperature as developed by internal chemical reaction.

3. That the experiments of Hittorf, Siemens, and others showing that gases do not glow at an average temperature of 1500° C. produced by external heating are no evidence that the same gases when produced in flames of the same average temperature are not veritably incandescent.

4. That if the heat of chemical combination be supposed to be stored in the products of combustion in a flame, the temperature of these products must be exceedingly high and probably high enough to produce luminosity.

5. That iodine vapour can be made incandescent by heating to temperatures below that at which glass is red-hot.

Part II.—*The Genesis of Flame-Spectra.*

I propose now to discuss some cases of flame-coloration in respect to the chemical reactions by which they are accompanied in the flame.

Sodium.—The characteristic yellow flame of sodium with the D line-spectrum represents, as is well known, the most easily obtainable flame-spectrum. It is yielded by all salts of the metal in the flame of coal-gas or hydrogen. It is quenched, according to Mitscherlich *, if hydrochloric acid be supplied in excess along with the sodium salt, which may be done by adding an excess of ammonium chloride to the bead.

The yellow tint is also, according to Mitscherlich, not yielded in the flame of hydrogen burning in chlorine when these gases are burnt in an oxy-hydrogen burner. I have repeated Mitscherlich's experiments with great care, using

* Pogg. *Ann.* cxvi. p. 499; also cxxi. p. 459.

the flame of hydrogen in chlorine and of chlorine in hydrogen. So long as any oxygen remains in the gases the flame shows a distinct yellow colour when a bead of a sodium salt is introduced into it. As the oxygen is removed by a current of purified gas (chlorine or hydrogen), the yellow colour fades until it is imperceptible to the eye. Viewed with the spectroscope the D line shows a corresponding diminution of intensity, and, in entire absence of oxygen, is doubtless extinguished. As I have only once succeeded in entirely obliterating it, I do not wish to speak positively. The fact that the red line of lithium is easily quenched under similar conditions confirms the belief that the same would be the case with the more sensitive sodium, if all traces of oxygen could be removed.

It appears to me that the above facts present great chemical anomalies and difficulties. If we are to make the common assumption that the yellow flame is due to sodium vapour, the element must be liberated either by dissociation by heat or reduction. Of dissociation by heat we have no independent evidence, and it is gratuitous to suppose that it should take place in a coal-gas flame and not in the flame of hydrogen burning in chlorine. If the process is one of reduction, we have to go beyond our experimental knowledge to suggest an explanation. Thus the liberation of sodium from common salt in a hydrogen-flame must be due either to the union of hydrogen with the chlorine to form hydrochloric acid and free sodium, or to the action of steam which forms hydrochloric acid and sodium hydrate or oxide, the latter being then reduced to the metal by the hydrogen. If it is said that hydrogen may decompose salt in the first way at high temperature, it must also be remarked that hydrochloric acid itself dissociates at high temperatures. If, on the other hand, the steam is the active agent, it is certainly taking a liberty to invoke its presence to act on the salt, and to ignore its probable interference with any reduction of the oxide or hydrate to be subsequently effected by hydrogen.

If we can explain the coloration of a hydrogen-flame by salt, it will of course be easy to explain it in the case of a coal-gas flame.

The suppression of the colour in a hydrogen-chlorine flame can only be explained from the point of view of reduction by assuming that the conjoint action of oxygen and hydrogen is necessary for the decomposition of the sodium chloride, the hydrogen taking the chlorine and the oxygen the sodium, the sodium oxide being thereupon reduced by hydrogen.

The only alternative to the above explanations is, so far as I am aware, that indicated by Arrhenius in his experiments on the electrolytic conduction of the heated vapours of salts (Wied. *Ann.* xlii. p. 18, 1891).

Arrhenius supposes that when salt is supplied to a flame, sodium hydrate is formed by the influence of steam and that the hydrate then undergoes partial ionic dissociation, the liberation of sodium taking place without the intervention of ordinary chemical action. The process is thus regarded as analogous to the dissociation of electrolytes in dilute aqueous solution. I cannot attempt to summarize the experimental evidence by which Arrhenius seeks to establish his interesting theory. If true, it would certainly remove many difficulties which have been met with in attempting to account for the phenomena of flame-coloration on purely chemical grounds *.

With regard to Arrhenius's view of the matter, I will only remark at present that the liberated sodium must sooner or later meet with oxygen, and burn. If the yellow light of the flame is due to the vibrations of ionic sodium, it would seem likely that the light emitted during combustion of the sodium, and due presumably to sodium oxide, should be different. Now the light from sodium burning in oxygen gives a continuous spectrum, and it is possible that the faint continuous spectrum which accompanies the line-spectrum of sodium salts heated in a flame may be due to the combustion of the sodium, whilst the line-spectrum is due to the mere vibration of the sodium ions.

The genesis of the sodium spectrum has recently been made the subject of experiment by Pringsheim (Wied. *Ann.* xlv. p. 428, 1892). He shows first of all that sodium carbonate and sodium chloride, when vaporized in a hot porcelain tube, give neither absorption nor emission spectra. Metallic sodium heated in the tube filled with nitrogen gives first a coloured vapour showing a banded spectrum, and then a transparent vapour exhibiting the ordinary sodium spectrum. He then raises the question whether this spectrum is dependent on temperature alone, or is caused by the act of chemical union

* In addition to those already pointed out I may adduce the following :—When a flame coloured by a bead of sodium salt is viewed against a bright background of D light, it is seen to be surrounded by a black mantle. If this is due to absorption by free sodium, then the element must be able to exist in an atmosphere of steam and carbon dioxide. This is utterly opposed to our ordinary notions of the chemical relations of the substances in question, but would present no difficulty from the point of view of Arrhenius.

of sodium with traces of oxygen lingering in the nitrogen and the oxygen contained in the siliceous material of the porcelain tube. To test this question he produces a "cool" flame by igniting a current of air charged with just enough vapour of carbon disulphide to give a combustible mixture. The average temperature of the flame is below 150° C. In this flame a fine spray of a sodium salt gives no spectrum; and he finds that not until enough additional carbon disulphide is supplied to give a much higher temperature does the spectrum appear. Comparing this result with the results of the porcelain-tube experiments, Pringsheim concludes that since in the latter case the sodium salts show no spectrum at temperatures which, in the case of a flame, suffice for the display of the spectrum, chemical action and not heat alone must be the cause of this difference; that, in short, flame-spectra of sodium salts are not due to simple dissociation by heat, but to chemical processes of reduction.

By way of confirming this conclusion Pringsheim then describes the effect of heating sodium salts in a hot porcelain tube in presence of different gases. In air, nitrogen, or carbon dioxide no spectrum is produced, but in hydrogen the D-line immediately appears. This is not quenched by the addition of carbon dioxide, but immediately disappears on the introduction of air. The reduction of the sodium salts and the production of a spectrum he also effects by iron and carbon. Finally, by an ingenious device, Pringsheim studies the phenomenon in another way. The sodium salt is introduced into the tube in a nickel or iron boat which can be suddenly removed from the hot part of the tube by an electromagnet. In the case of the iron boat the iron acts also as a reducing agent. The point is to see whether, having developed the spectrum with the iron boat in the hot part of the tube (filled with hydrogen), this spectrum fades suddenly or gradually when the boat is withdrawn to the cold part of the tube. If it fades gradually the conclusion is that the liberated sodium vapour is luminous *per se,* and only ceases to give a spectrum as it migrates to the cool part of the apparatus. If the spectrum fades suddenly the conclusion is that the spectrum is only evinced at the moment of liberation of the sodium from its compound, and is therefore the direct result of chemical action. The latter Pringsheim finds to be the case.

Pringsheim then summarizes his conclusions as follows:—

1. There is no gaseous source of light which satisfies the conditions of Kirchhoff's law.

2. Glowing gases can be obtained of a temperature below 150° C. (cold flames).

3. Sodium salts emit light in flames only as a consequence of chemical processes.

4. Metallic sodium heated in neutral gases emits light only as a consequence of chemical processes.

5. The assumption that gases can emit light by mere elevation of their temperature is a hypothesis demanded neither on experimental nor theoretical grounds.

These conclusions, which go to the root of spectrum analysis, are, it must be admitted, of the most serious importance. I am not satisfied that they are warrantable, and wish to direct attention to the following points:—

(I.) The fifth, and in all probability the first, conclusion (*supra*) of Pringsheim is contradicted by the experiment with iodine vapour which I have already described (p. 252).

(II.) The second conclusion of Pringsheim is unwarrantable, for the reasons stated in the first part of this paper. It may be that a certain disulphide air-flame can be obtained having an average temperature below 150° C. This tells us nothing of the temperature of the molecules of CO_2 and SO_2 which are formed in the flame. Theory, on the other hand, would assign to them a very high temperature if the heat produced in their birth is assumed to be stored in them for an instant. The ready inflammability of the mixture only points to the relatively great distance at which the combining molecules of CS_2 may be apart, and to the interpolation of a large number of non-burning molecules which tend enormously to lower the average temperature of the flame.

(III.) Pringsheim's third and fourth conclusions are undoubtedly the most serious. Metallic sodium, he says, heated in neutral gases emits light only as a consequence of chemical processes. This conclusion is reached only by indirect evidence. In the first place, I would remark on the fact that according to Pringsheim (*loc. cit.* p. 444) the admission of carbon dioxide to the hot porcelain tube, in which the sodium spectrum has been developed by the action of hydrogen on sodium compounds, does not destroy the spectrum, while air does so immediately. Why is this? Hot sodium vapour and carbon dioxide are quite incompatible; surely CO_2 and air ought both to extinguish the spectrum; both are powerful oxidizing agents to sodium. The important experiments are those with the movable iron or nickel boat, and in these another difficulty with CO_2 appears. After withdrawing the

iron boat from the hot part of the tube filled with CO_2, the spectrum does not fade to the degree anticipated but acquires a stationary intensity. This is attributed to the lingering of sodium vapour, which attacks the sodium silicate with which the interior of the tube has become coated in previous experiments. A " reciprocal " reaction is said to take place : the sodium vapour attacks the silicate, liberating other sodium vapour, a process at first rapid but gradually attaining equilibrium. After this the process goes on steadily, sodium liberating sodium. This seems to me to be a very extraordinary assumption, and more a robbing of Peter to pay Paul than the picture of a chemical equilibrium. We are to suppose that a film of sodium silicate—at the most, liquid—in contact with sodium vapour, and above all in an oxidizing atmosphere of carbon dioxide, is constantly giving and taking sodium atoms so as to keep up the chemical action which Pringsheim demands for the development of the sodium spectrum. Such a state of things will be, I imagine, as surprising to chemists as it is novel. It is true that dissociation phenomena are pictured as involving a constant in-and-out movement of the products of dissociation from the compound undergoing dissociation. But if sodium acts on sodium silicate at all it will be to liberate silicon, and after that is complete we can only assume the resulting sodium oxide to react with fresh sodium at the temperature at which sodium oxide dissociates. We have no knowledge of the dissociation of sodium oxide. If, as I venture to think, Pringsheim's explanation of this point is not to be accepted, there is less difficulty in accounting for his other observations, for the sudden reduction of the intensity of the spectral effect in hydrogen when the boat is suddenly withdrawn is only important in comparison with what occurs in CO_2. I do not see any cause for surprise that the intensity of the spectrum should suddenly diminish in hydrogen when the boat is withdrawn suddenly. One would expect the moving boat to drag its small atmosphere of sodium vapour with it to the cool part of the tube,—and, again, one would not expect the spectrum to persist in air. I can, therefore, see no adequate grounds for the important conclusion which Pringsheim draws from these experiments, namely, that metallic sodium only gives its spectrum when undergoing chemical change.

I may summarize the views above expressed as follows :—

1. There is no evidence for, but much against, the supposition that sodium salts when introduced into a flame are dissociated by heat so as to liberate the metal.

2. There is great difficulty in accounting for the reduction of the metal by purely chemical processes.

3. Arrhenius's hypothesis of ionic dissociation in flames is a chemically acceptable way of accounting for the liberation of sodium when its salts are heated in flames.

4. There is no direct evidence and no decisive indirect evidence that the sodium spectrum is the direct consequence of the chemical action in which the atoms are engaged.

Postscript.

In a recent number of Wiedemann's *Annalen* * there is a paper by Paschen in which he shows by bolometric measurements that the invisible spectra of hot gases exhibit distinct maxima of intensity—that, in short, gases do give discontinuous spectra on being heated, independently of chemical action. On these grounds and others, some of which are similar to those explained in the foregoing paper, Paschen does not consider that Pringsheim's conclusions can be accepted.

XXIII. *Researches in Acoustics.*—No. IX.   *By* ALFRED M. MAYER, *Ph.D.*†

CONTENTS.

1. *On the Law connecting the Pitch of a Sound with the Duration of its Residual Sensation.*

IN October 1874 I published in the American Journal of Science Paper No. 6 of Researches in Acoustics, which contained an account of my attempts to establish the law connecting the pitch of a sound with the duration of its residual sensation. The law given in that paper was the expression of the results of the first experiments, extending through several octaves, ever made on the duration of sonorous sensations.

Subsequently, in April 1875, I published in the American Journal of Science ‡ the results of similar experiments which

* Vol. 50. p. 409 (1893).

† Communicated by the Author.

‡ The papers cited above were published in the Philosophical Magazine of May 1875, in one paper, "Researches in Acoustics, No. VI."

Madame Ema Seiler had made at my request. She made a long series of experiments with the same apparatus I had used. Her determinations, though agreeing with mine in having approximately the same variation of the residual sensation with the pitch, yet differed considerably in the absolute quantities which she found for the durations of these sensations. That the two series of observations should differ was to be expected from the known variation of the sonorous sensations among different observers; but the principal cause of the difference is to be attributed to the apparatus (fig. 3) used in these experiments. This apparatus generated sounds in addition to the one to be specially observed, so that the determinations were difficult to make except by one whose hearing was peculiarly trained and naturally gifted in the power of excluding other sound-sensations from the one alone to be studied. In the ability to analyse composite sounds Madame Seiler was noted; and I had no doubt at the time of the publication of her results that they were more worthy than mine to form the basis of a physiological law. This I stated in my paper of 1875, and the experiments described in the present paper, made with improved methods, show that the opinion then entertained was correct.

That there is a physiological law which gives the relation between the pitch of a sound and the duration of its residual sensation is shown by the numerous experiments contained in this paper. But those published in 1874 and 1875 sufficed to establish that fact; yet those experiments have never been repeated by physiologists.

I have waited nineteen years in the hope that others would make similar experiments, so that the combination of the results of various experimenters would give an expression of the law which might be regarded as general and accepted as expressing the average residual sensations of sounds.

It is true that Professor C. R. Cross and H. M. Goodwin published a series of similar experiments in "Some considerations regarding Helmholtz's Theory of Consonance" (Proc. Amer. Acad., Boston, June 1891). They obtained the smallest consonant intervals of simple sounds by blowing sheets of air across the mouths of resonators. The reciprocals of the differences of the frequency of the vibrations forming the intervals thus found are plotted in the curve C C of fig. 1. I and I' give their determinations of the durations of the residual sensations of UT_3 and of UT_4, deduced from their observations of the coalescence of these sounds when interrupted by a perforated disk rotating between a resonator and its corresponding fork.

The curve S shows Madame Seiler's determination of the residual sonorous sensations ; M shows mine. It is evident that the meandering, undecided curve, C, cannot be the expression of a law, and that the data I and I' cannot be combined with those contained in the curve S, or in the

Fig. 1.
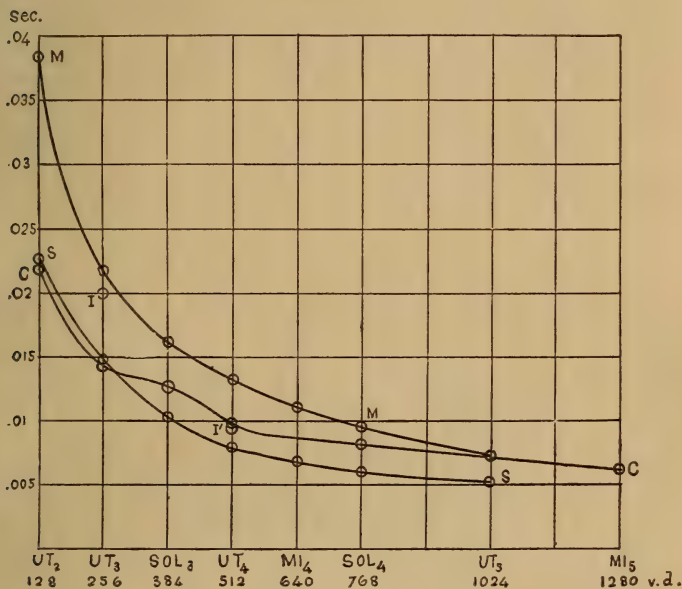
curve M. In a general way the curve C shows that the smallest consonant interval of two tones contracts as the pitch of the tones, forming the interval, rises.

The physicists Mr. Alexander J. Ellis and Professor J. A. Zahm have discussed the bearing of the law (as given by the experiments of 1874 and 1875) on the elucidation of many facts in consonance and dissonance, to which I referred in my paper of 1874*.

On the Duration of the Residual Sonorous Sensation.

The duration of a residual sonorous sensation is really the duration of the entire period in which a sensation of sound is perceived after the vibrations outside of the ear, giving rise to that sensation, have ceased to exist. While the total

* See Ellis's translation, of 1875, of Helmholtz's *Die Lehre von den Tonempfindungen,* pp. 173, 701, 795, and Ellis's "Illustrations of Just and Tempered Intonation," Proc. Musical Assoc. of London, June 7, 1875; Zahm, ' Sound and Music,' Chicago, 1892.

duration of the after-sensation produced by the stimulus of light can be measured, as in the case of an electric flash, the determination of the total duration of the after-sensation of a sound appears, in the light of our present knowledge and with the means of experiment at our command, to be a problem very difficult to solve.

The object of this research was not to determine the total duration of the after-sensation of a sound, but to measure that duration in which the after-sensation of a sound does not perceptibly diminish in intensity.

Fig. 2.

In fig. 2, D and E represent openings in a screen impervious to sound. The distance between the openings equals thrice the diameter of an opening. A tube, R, having the same interior diameter as the openings, is supposed to convey sound-vibrations against the screen, while the tube itself moves from left to right with its mouth sliding along the surface of the screen. In the position A, the sound is just about to traverse the opening D to the ear on the other side of the screen. As R progresses over the opening D, the sound traverses the opening till R has reached the position F B. Then, in the path of the tube from B to C, no sound traverses the screen. When the edge B of the tube has reached the position C, the sound is again just on the eve of traversing the screen through the opening E. As the distance A to B equals B to C, the periods during which the sound traverses the screen equal those in which it does not do so. If these alternations of sound and silence should succeed one another so rapidly that the sensation of the sound is uniform in its intensity, it may at first sight appear that during the time that the tube takes to go from B to C the after-sensation of the sound has not diminished in intensity. But is B to C to be taken as the measure of the duration of uniform sensation? As the tube R moves over D a sound with a varying intensity traverses the opening in the screen. We cannot suppose that the residual sensation caused by the stimulus of the sound traversing a minute opening in the screen equals that caused by the sound which traverses the screen when the circles R and D coincide. In such experiments, however, we are driven to take as the duration of the

undiminished residual sensation the time that the centre of the tube, R, takes to go from the centre of D to the centre of E.

In this illustration I have, for simplicity and conciseness, supposed the tube R to move over the openings D and E. In the actual experiments D and E are two of several holes in a disk, arranged in a circle, and the disk rotates while the tube R is fixed. Another tube placed in the prolongation of the tube R, on the other side of the disk, conveys the interrupted sound to the ear.

Evidently the manner in which the tube conveying the sound to the disk is open and closed by the revolving disk has to be considered in researches made with this apparatus. I give two cases whose discussion has led me to modify,

Fig. 3.
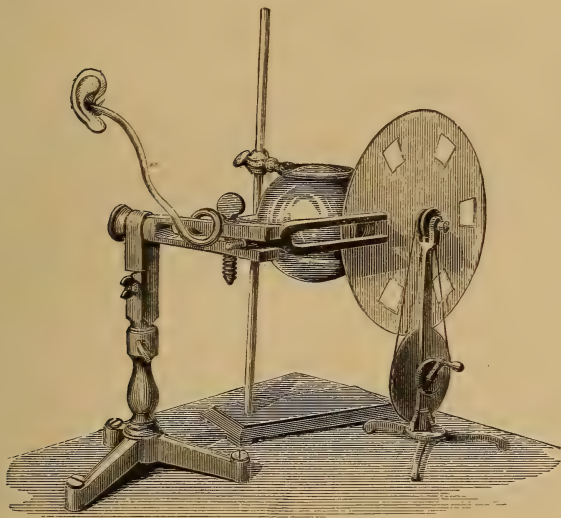
with marked efficiency, the apparatus, shown in fig. 3, which was used in the researches published in this Journal in 1875. In that apparatus the interruptions of sound were made by a perforated disk revolving in front of the mouth of a resonator, while the interrupted sound was conveyed to the ear by a tube attached to the small opening in the nipple of the resonator.

This mode of obtaining the interruptions of the sound is objectionable because the resonator is not in tune with the fork except when the former is fully opened, and also because

the perforated disk rotating across the mouth of the resonator gives rise to two secondary sounds and a resultant sound, fully described in my paper of 1875 [*]. These sounds, from their intensity in this form of experiment, mask the proper sound of the fork, making the determination of the durations of the sonorous sensations both difficult and uncertain. Also, in these experiments the action of the interrupted sound on the ear is distressing, even injurious; for the hearing of one of my ears was permanently impaired by the experiments I made with this apparatus nineteen years ago.

In the apparatus presently to be described, the fork vibrates in front of the mouth of the resonator, and the interruptions in the flow of sound are caused by the perforated disk revolving in front of the small opening in the nipple of the resonator, as shown in fig. 7.

Discussion of the Effects of the Relative Sizes of the Openings in the Revolving Disk and of the Opening in the Tube conveying the Sound to the Disk.

First Case. Suppose that the opening of the nipple of the resonator and the openings in the disk have the same diameter. In the actual experiments these openings were 1 centim. in diameter. The nipple of the resonator had a tube of that diameter adapted to it.

Fig. 4.
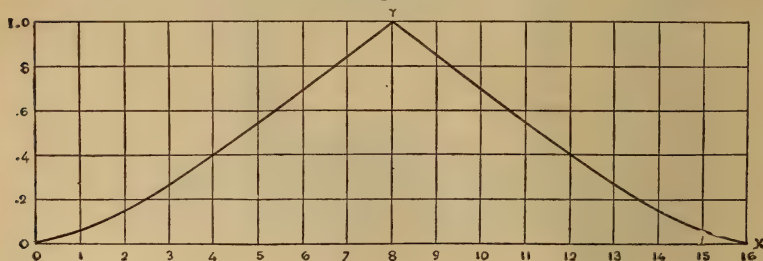
Fig. 4 is the graphic representation of the results of computing the varying areas of the opening of the tube of the resonator, as an opening in the disk passes in front of it. This diagram is to be studied in connexion with fig. 2. The entire length on the axis of abscissas OX gives the space A to B of fig. 2, divided into sixteen parts. The ordinates of the curve give the relative areas of opening for corresponding positions on the axis of abscissas. The ordinate

[*] See a paper by Lord Rayleigh, "Acoustical Observations, III. Intermittent Sounds," Phil. Mag., April 1880, in which the author gives an explanation, in mode and in measure, of the secondary sounds and of the resultant sound, observed by me in these experiments.

marked 8 Y shows the full area of opening when the circles of the tube of the resonator and of the disk coincide. It will be observed that the tube is opened and closed slowly, and is only instantaneously fully opened at 8.

Second Case. The openings in the disk remain 1 centim. in diameter, but the opening in the nipple of the resonator is $\frac{1}{2}$ centim. in diameter. Fig. 5 shows the relations between the areas of opening of the nipple of the resonator and the

Fig. 5.
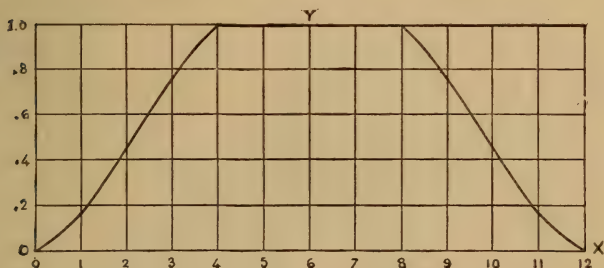
path A to B (fig. 6) of this opening, R, as it is supposed to move across the opening D in the disk. Fig. 5 is to be studied in connexion with fig. 6. Fig. 5 shows that the opening and closing of the nipple of the resonator take place rapidly, and that the nipple remains fully opened from 4 to 8, that is, during one-third the time that the opening in the disk takes to traverse the opening in the resonator. The advantages gained by this mode of experimenting are considerable. The periods of sound and of silence are sharply marked, and, as we shall now show, the fact that the hole in the resonator has half the diameter of the hole in the disk gives us the means of approaching nearer to the measure of the veritable time during which we have an after-sensation of uniform intensity.

Fig. 6.

In fig. 6 R represents the opening in the nipple of the resonator, supposed to pass over the opening D in the disk. In this case, as in fig. 2, the space A to B in which sound traverses the revolving disk is equal to the space B to C in which silence supervenes, for the distance separating two holes in the disk equals twice the diameter of a hole, or four

times the diameter of the hole in the nipple of the resonator. But in this form of the experiment we are again in doubt as to what space should be taken as measuring the duration of the uniform residual sensation. The period from the full opening of the resonator in one position to the full opening in the succeeding one is equal to the time the disk takes to go from G to H, which is equal to the distance D to E between the centres of the openings in the disk minus the diameter of the opening in the resonator, or, DE minus $\frac{1}{6}$ DE. This distance, G to H, evidently measures the periods between maximum and maximum intensities of succeeding sound-pulses; and we have taken this distance, in terms of velocity of rotation, as the measure of the period of uniform residual sound-sensation, because we have no certain knowledge of the relative durations of the residual sensations corresponding to vibrations which pass the disk with increasing intensity, from 0 to 4, fig. 5, and with decreasing intensity, from 8 to 12.

In our experiments we measured the number of flashes of sound entering the ear by knowing the number of revolutions of the disk per second, and the number of holes in the disk. From this knowledge we compute the time it took the disk to go over D to E in fig. 6, the distance between centres of two neighbouring holes; then we reduced this time by one sixth, which is the ratio of the diameter of the opening in the nipple of the resonator to the distance D to E, and took this reduced time as the duration of the uniform residual sensation. The duration of the sonorous sensation determined in this manner is evidently nearer the truth than that obtained with apparatus in which the hole in the tube conveying the sound to the disk and the holes in the disk have the same diameter.

The Apparatus and Methods used to Measure the Durations of Residual Sonorous Sensations.

[A.] I shall first describe the apparatus which I found the most efficient for these measures, and then describe three other forms of apparatus used.

In fig. 7 is seen a perforated disk mounted on the axle of a rotator. In front of the disk is the resonator with its nipple close to the surface of the disk. A tuning-fork is opposite the mouth of the resonator. On the other side of the disk, with its axis in line with the axis of the nipple of the resonator, is the tube which conveys the interrupted sounds to the ear. The opening in this tube has the same diameter as the openings in the revolving disk. Behind the line of this tube is seen, on the end of the axle, a fly-wheel of copper weighing a kilogramme.

The bevelled face of the driving-wheel of the rotator has three grooves cut in it, in steps. Corresponding grooves are cut in the pulley of the axle.

To run a rotator of this description smoothly, without jars or vibrations, it is necessary that the cord which passes over the driving-wheel and pulley should be very flexible and have a circular section of uniform area throughout its length.

Fig. 7.
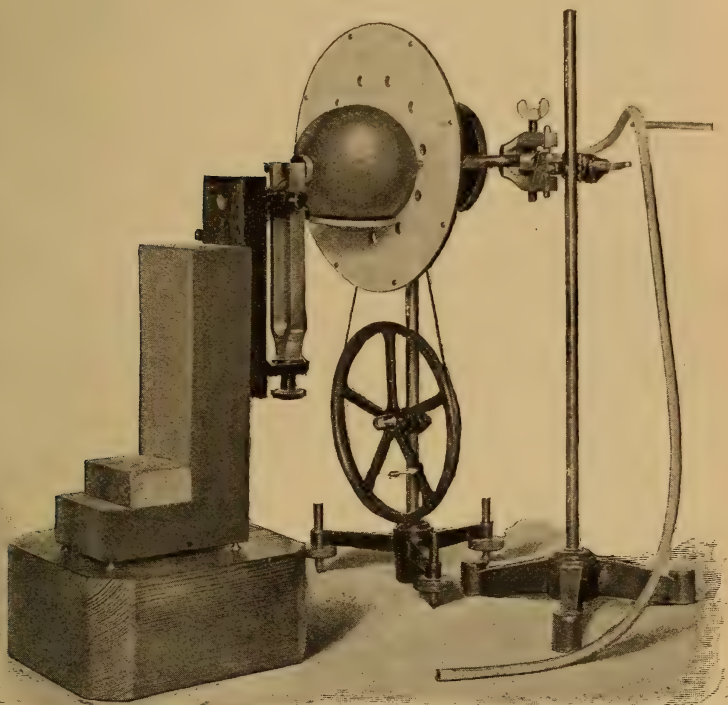
I obtained such a cord by soaking a cord of porpoise leather in neat's-foot oil, and then drawing it many times through wire-drawing plates. The ends of the cord are connected by a short hook-and-eye coupling. The driving-wheel can be slipped up or down the standard of the rotator to adjust the tension of the cord.

The driving-wheel is turned by a handle of aluminium of the form shown in the figure. It is necessary to have a handle of small diameter in order to turn the wheel with a uniform velocity. The fingers which clasped the handle were coated with plumbago dust.

In all the experiments the driving-wheel of the rotator was revolved either once in a second or twice in a second. This is accomplished, after some practice, in the following way :— The rotator, on which is mounted the disk and fly-wheel, is placed near a clock giving loud beats of seconds, and the driving is revolved by the guidance of the hand and ear. The results of the experiments showed that the velocities thus given to the disk were sufficiently uniform, and the measures of the durations of sonorous sensations sufficiently concordant and precise to obtain the data of the physiological law.

I adopted this method of rotation in preference to mechanical means for controlling and measuring the revolutions of the disks. To determine when the interrupted sounds have blended requires, so to say, a flexible apparatus whose velocity is under the immediate control of the hand and ear. This is important in making the final judgement between sounds, one of which appears to have too few interruptions, the other a few more interruptions than are necessary to give a continuous uniform sensation. It is evident that when we can at once slightly increase or diminish the velocity of rotation of the disk, we have the means of making comparisons rapidly succeeding one another. A rotator, driven as described, forms more a part of the observer than one driven and regulated by mechanism.

As there were three grooves in the driving-wheel and three in the pulley on the axle, and as the driving-wheel was revolved either once or twice in a second, eighteen different velocities could be given to the rotating disk.

Disks were made having numbers of holes from 5 to 19, so that, with 18 velocities and the various numbers of holes in the disks, it was easy to select a disk, driven with a known velocity, which gave the exact number of interrupted sounds per second to blend.

The 18 ratios of velocities of the driving-wheel and of the pulley on the axle of the rotator were obtained as follows :— A circle of cardboard, divided into one hundred parts, was clamped on the rotator in front of a disk. The driving-wheel was rotated either once or twice in a second, so that the conditions were the same as in the experiments. From 10 to 100 revolutions of the driving-wheel were made before the ratio was determined. The division to which a fixed index pointed on the divided circle gave the fraction of a revolution. The whole number of revolutions was given by a simple counter which moved with very little friction.

The rotating disks were made of mahogany, 5 millim. thick, with disks of cardboard about 2 millim thick screwed to the wooden disks. The circumferences of the holes in the wooden

and cardboard disks exactly coincided. The circle of holes in the disks was placed 5 centim. from its border. The rotator and disks were so carefully made that the nipple of the resonator was only $\frac{3}{10}$ millim. from the surface of the revolving disk. The mouth of the tube conveying the interrupted sounds to the ear was about the same distance from the surface of the other side of the disk. The disks were clamped on the axis of the rotator between smaller flat disks of brass, not shown in the figure.

The diameter of the holes in the disk, and of the interior of the tube conveying the sounds to the ear, was 1 centim. The diameter of the opening in the nipples of the resonators was $\frac{1}{2}$ centim.

The disks were made of mahogany which had been in my possession for thirty years. It was well seasoned and had nearly the thickness required for the disks. This wood was used because it holds the form given it better than any wood I have had experience with.

Sound passes through mahogany and other woods even when a centimetre in thickness. Sound also passes through cardboard, but not so readily as through wood. I found that by placing cardboard on wood I formed a screen of heterogeneous materials which presented an effective obstruction to the passage of sound.

Fig. 8.
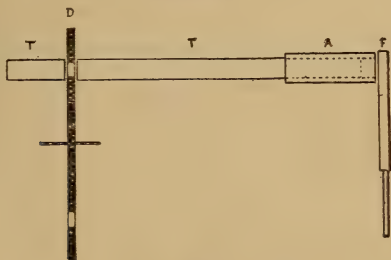
[B.] In the second form of apparatus I replaced the resonator by resonant tubes as shown in fig. 8, where F is the fork, T the tube, with a tube of larger diameter, A, sliding on T, so that the air in the tube could be adjusted to vibrate with the fork. On the other side of the disk D is the tube T′, to which is attached the tube of caoutchouc which leads to the ear. This arrangement is like that used by Dr. R. Kœnig, and described on page 140 of his *Quelques Expériences d'Acoustique*, Paris, 1882, and used by him for the observation of the sounds produced by interruptions of continuous sounds.

Experiments made with this apparatus gave the same results as those made with apparatus [A], but the sounds given are so feeble compared with those coming from the resonator (fig. 7), that the periods of sound and silence (or, rather, of sound and much diminished sound) are not sharply separated. It followed that the judgment of a continuous sensation on the ear could not be so neatly made with the use of the resonant tubes as when the resonators were employed.

[C.] To obtain sharper demarcation of sound and silence by having no aperture for the lateral escape of sound between the rotating disk and the nipple of the resonator and between the disk and the tube conveying the sound to the ear, I made the following apparatus (fig. 9). I turned disks of brass flat and of uniform thickness. These disks were revolved on a rotator driven by gear wheels made of "fiberoid," so that the movement should be noiseless. The number of teeth on the wheels and holes in the disks were such that I was enabled to make three determinations corresponding in the number of interruptions of sound to those already obtained with apparatus [A].

Two brass tubes, T and T′, fig. 9, one having an interior diameter of $\frac{1}{2}$ centim., the other an interior diameter of 1 centim., slid accurately and with little friction in two tubes,

Fig. 9.
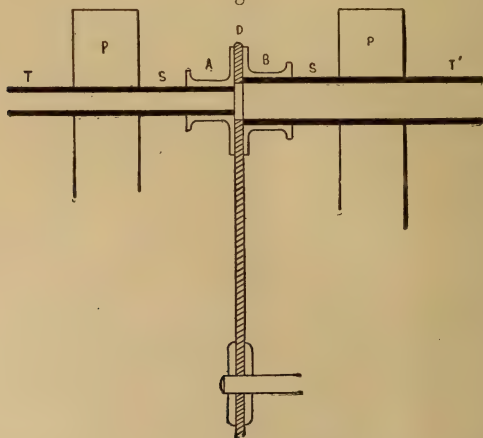
A and B, with flanges on their ends. These flanges were pressed against the surfaces of the disk D by two delicate helical springs fitting over the tubes at S and S′, between the flanges of A and B and the standards P and P′. The tubes T and T′ were as close as possible to the disk while it rotated. The flanges A and B were of such diameter that no sound

could issue between them and the surfaces of the rotating disk, because the flanges entirely covered the hole in the disk while this hole traversed the tubes T and T'. A tube of caoutchouc led from the tube T' to the ear.

Although a film of oil was between the flanges and the disk, and the disks were so accurately made that the greatest departure from uniformity of thickness amounted to only $\frac{1}{25}$ millim., yet the sounds produced by the sliding of the disk between the flanges caused much distraction in the perception of the sound from the resonator, which was adapted to the tube T, of $\frac{1}{2}$ centim. in diameter. The results obtained with this apparatus agreed with those given by apparatus [A].

[D.] I had formed great hopes of having the best apparatus for the determination of the duration of a residual sensation in

Fig. 10.
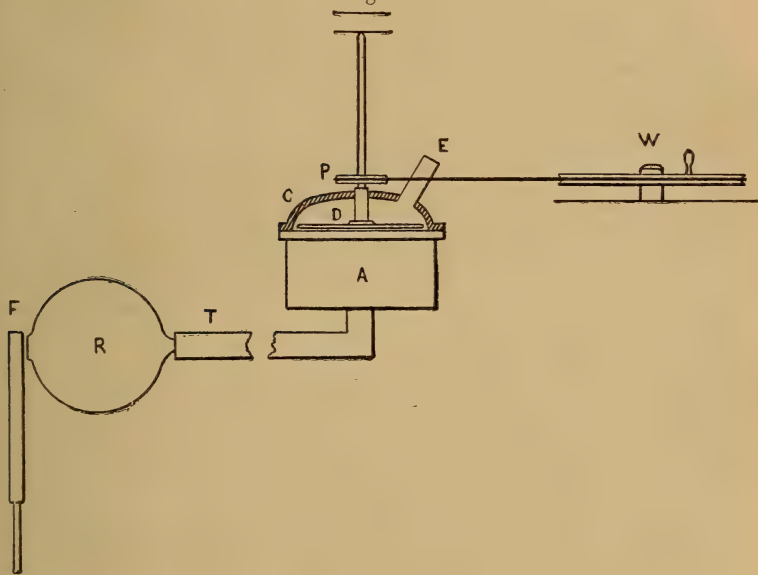
the one shown in fig. 10. A is the lower drum of a Helmholtz double siren; D, the perforated disk of the siren, which was rotated by the driving-wheel W. The disk D was enclosed in a cover, C, of the form shown in fig. 10, clamped to the drum of the siren. The sound issued from the box thus formed, and was conveyed to the ear by the tube E, to which was attached a tube of caoutchouc. The sound to be experimented on was conveyed from the fork, F, and resonator, R, through a long tube, T, to the drum of the siren. By placing pulleys, P, of various diameters on the axle of the disk of the siren, and by opening one or another of the various circles of holes in the drum A, I had

the means of obtaining a considerable range in the number of interruptions of sounds per second.

The results given by this apparatus were the same as those obtained with [A], but the objection to its action is the production of sounds by the apparatus itself, caused by the rotation of the perforated disk. These sounds distracted the attention from the phenomenon of the continuous sensation produced by the interruptions of the sound from the fork, and so masked it that I consider this apparatus the least efficient of those I have described.

These experiments on the blending of interrupted sounds are not pleasant to make. The ear soon becomes fatigued, and the perception of sound is dulled. After an experiment the ear has to be rested during a considerable time before the experiment can be repeated satisfactorily. Thus much time is consumed, and these experiments cannot be made in a few days, but weeks are required to arrive at satisfactory measures; also, considerable time is consumed in gaining mastery over the apparatus. To make these experiments less tedious, fatigue of the ear is to be avoided. This is done by not allowing the interrupted sounds to enter the ear longer than during two or three seconds; then a rest of five to six seconds is taken, while the fork is kept in action and the disk revolved with the same velocity; then another three-second period of sound is given the ear. This is best done by placing the rubber tube in the meatus of the ear and pinching the tube between the fingers. By relieving the pressure more or less we can regulate the intensity of the sound which enters the ear, or we can shut the sound off. The other ear is tightly closed with beeswax softened with a little turpentine.

Within the limits of the intensities of sound used in these experiments, I found no change in the duration of the sensation with change in the intensity of the sound. It seems probable that such connected changes exist. If they do exist, then it would appear, from the smoothness of the curve I have obtained from the experiments, that the relative mean intensities of the sounds used did not vary sufficiently to make apparent any change in the duration of the after-sensation with change in the intensity of the stimulus.

Table of Results of Experiments.—The Empirical Formula which gives the Relation of the Pitch of a Sound to the Duration of its Residual Sensation.

The results of the experiments made with the various forms of apparatus just described are given in the following Table I.

TABLE I.

A.	B.	C.	D.	E.	F.	G.	H.	I.	K.	L.
UT₁	64	23·1	$\frac{1}{26·9}$	·0361	·0369	+·0008	.....	.....	.....	1·38
UT₂	128	36	$\frac{1}{43·2}$	·0231	·0228	−·0003	·0280	·0324	+·0044	1·77
SOL₂	192	....	.....	.....	.....	.....	·0232	·0237	−·0001	2·06
UT₃	256	62	$\frac{1}{74·4}$	·0134	·0133	−·0001	·0190	·0189	−·0002	2·12
MI₃	320	73	$\frac{1}{87·5}$	·0114	·0112	−·0002	·0160	·0158	−·0001	2·18
SOL₃	384	88	$\frac{1}{105·6}$	·0094	·0097	+·0003	·0137	·0137	·0000	2·37
UT₄	512	108	$\frac{1}{130}$	·0077	·0078	+·0001	·0110	·0109	−·0001	2·53
MI₄	640	126	$\frac{1}{161·2}$	·0066	·0067	+·0001	·0092	·0092	·0000	2·68
SOL₄	768	143	$\frac{1}{171·6}$	·0058	·0059	+·0001	·0080	·0081	+·0001	3·01
UT₅	1024	170	$\frac{1}{204}$	·0049	·0049	·0000	·0066	·0066	·0000	
MI₅	1280	....	.....	.....	.....	.....	·0057	·0057	·0000	
SOL₅	1536	....	.....	.....	.....	.....	·0052	·0052	·0000	
UT₆	2048	....	.....	.....	.....	.....	·0045	·0044	−·0001	
MI₆	2560	....	.....	.....	.....	.....	·0039	·0039	·0000	
SOL₆	3072	....	.....	.....	.....	.....	·0036	·0036	·0000	

Column A gives the names of the sounds, and B the numbers of their vibrations (v.d.) per second ; C, the number of beats of interrupted sound received by the ear in a second to blend into a continuous uniform sensation. In column D are the durations of the residual sonorous sensations, expressed in vulgar fractions. The numbers in column D are obtained, as already explained, by diminishing the reciprocals of the numbers in column C by $\frac{1}{6}$. Under E are the fractions in column D in decimals. Under F are the durations of the residual sensations, computed by the formula

$$D = \left[\frac{33,000}{N+30} + 18\right] \cdot 0001,$$

in which D equals the duration of the residual sensation given by a sound of N number of vibrations per second. Under G are the differences between the computed and observed values of the residual sensations. These differences are so small, except in the case of SOL_3, that we may adopt the empirical

Fig. 11.
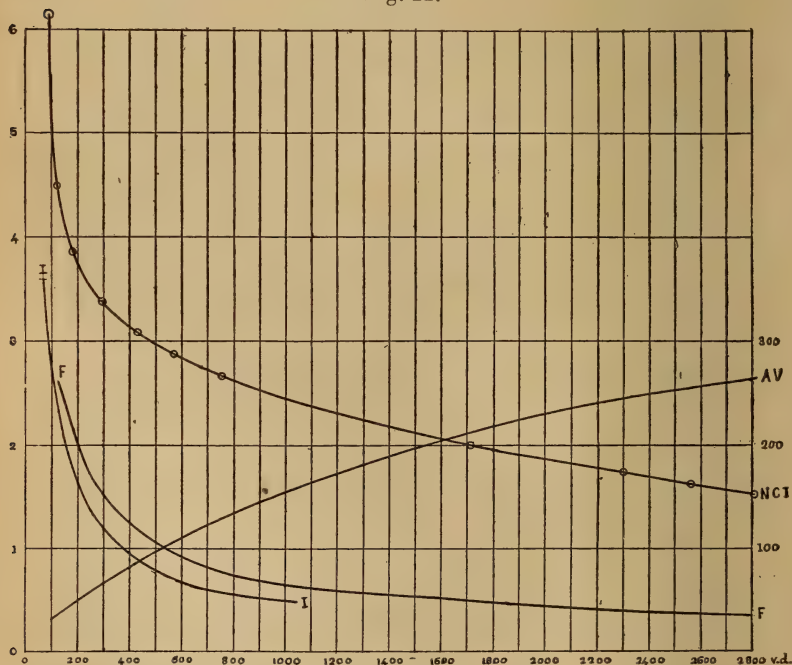
formula as expressing the law which connects the pitch of a sound with the duration of its residual sonorous sensation.

This formula, however, only refers to my own auditory sensation. It is a physiological law; and I imagine that the durations of these residual sonorous sensations will vary more with different observers than do analogous visual sensations. It is therefore to be wished that others will repeat these experiments and obtain determinations which, when combined, will give a law which may be accepted as the expression of the average durations of the residual sonorous sensations.

The results in column E are given graphically in the curve I of fig. 11. The unit on the axis of abscissas is 100 v.d. The unit on the axis of ordinates is ·01 second.

The determination of the duration of the residual sensation of UT_1 [64 v.d.] was very carefully made, and made many times. The experiments gave ·0361 second for the duration of this sound. The formula gives ·0369, which is $\frac{1}{45}$ greater than the observed duration. The greatest difference existing between the observed and computed duration of the remaining sounds of the table is in the case of SOL_3 [384 v.d.], where the computed is $\frac{1}{31\cdot3}$ greater than the observed duration.

In column L of Table I. are given the number of wave-lengths of the sounds which pass into the ear through a hole in the rotating disks when these interrupted sounds blend into uniform sensations. The average number of wave-lengths which pass a hole is about $2\frac{1}{4}$. As the sound rises in pitch, more wave-lengths pass the hole; thus, while only 1·38 wave-length passes in the case of UT_1, three wave-lengths pass in the case of UT_5.

An examination of fig. 6 shows that sound passes to the ear while a hole in the disk passes over three diameters of the hole in the nipple of the resonator, while the distance between the centres of neighbouring holes in the disk equals six diameters of the hole in the resonator. Hence, to ascertain the number of wave-lengths which enter the ear during the passage of a hole in the disk across the hole in the resonator, we must divide the number of vibrations per second of the sound, given in column B, by twice the corresponding number in column C.

2. *On the Smallest Consonant Intervals among Simple Tones.*

When two simple tones which differ slightly in pitch are sounded simultaneously, beats are produced, which become more frequent as the difference in pitch increases, and with

this increase in the interval between the tones the dissonance becomes harsher, reaching a maximum dissonance when the number of beats are about $\frac{4}{10}$ of the number required to blend, then becoming less dissonant as the interval increases till, at last, the two tones blend into a consonance. These are the phenomena observed from SOL_1 [96 v.d.] to the highest tones used in music.

Having the law which gives the number of beats (produced by the interrupted sounds of tones of various pitch), which blend, one might naturally infer that the smallest consonant interval could be computed by that law. Given the pitch of a tone, we compute by the law the number of interruptional beats of this tone which blend, and adding this number to the frequency of the given tone we should apparently have the pitch of the upper tone which makes with the lower the smallest consonant interval*. This, however, is not so. Take, for example, UT_3 [256 v.d.]. The number of interruptional beats of this sound which blend is 62, and $256 + 62 = 318$, which, according to the law, should make a consonant interval with UT_3. But experiment shows that a tone of $256 + 58 = 314$ v.d. forms the nearest consonant interval with UT_3.

To render less tedious the comprehension of the results of many experiments on the smallest consonant intervals among simple tones, I shall at once give a table (Table II.) of the results of these experiments, and then give the account of the experiments that furnished the data of the table.

In column A are given the lowest tones of the consonant intervals which were experimented on. In column B are the number of vibrations to be added to the tones of column A to form the higher note of the smallest consonant interval, as deduced from the experiments on the duration of the residual sensations of interrupted sounds. In column C the numbers of vibrations by which the tones in column A have really to be increased to form the higher notes of the smallest consonant intervals. In column D are the numbers of vibrations to be added to those of column A to form the smallest consonant intervals as computed by the formula

$$N : N + \cfrac{1}{\left(\cfrac{42500}{N+23} + 23\right) \cdot 0001},$$

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* Rigorously, we should take in the computation the number of beats which blend corresponding to a sound of a pitch which is the mean of the pitch of the lower and upper sounds of the interval.

TABLE II.

Number of Experiment.	A. Tones.	B. Number of additional v.d. to form the smallest consonant interval as deduced from the experiments on the residual sensations of interrupted sounds.	C. Number of additional v.d. really required to form the smallest consonant interval.	D. Number of additional v.d. required to form the smallest consonant interval according to the formula $N : N + \left(\frac{42500}{(N+23)+23}\right)\cdot 0001 - 1$	E. Difference between D and C.	F. Smallest consonant intervals in semitones of equal-tempered scale.
[1]	SOL₋₁ [48]	19·0	No consonant interval.	16·0	.....	None.
[2]	UT₁ [64]	23·1	No consonant interval.	19·5	.....	None.
[3]	SOL₁ [96]	30·7	41	26·3	−14·7	$\frac{15}{100}$ semitones.
[4]	UT₂ [128]	36·0	38	32·8	−5·2	$\frac{1}{42}$ "
[5]	SOL₂ [192]	49·7	48+	47·4	−0·6	$\frac{86}{100}$ "
[6]	UT₃ [256]	62·0	58	57·0	−1·0	$\frac{53}{100}$ "
[7]	MI₃ −[316]	72·0	68	67·4	−0·6	$\frac{34}{100}$ "
[8]	LA₃ −[432]	91·2	85·4	85·9	+0·5	$\frac{12}{100}$ "
[9]	RE₄ −[575]	113·3	107·4	106·3	−1·1	$\frac{95}{100}$ "
[10]	SOL₄ −[766·2]	137·8	129·8	130·1	+0·3	$\frac{70}{100}$ "
[11]	LA₅ [1706·6]	219·3	210·4	212·0	+1·6	2 "
[12]	RE₆ [2304]	251·4	245	242·3	+2·7	$\frac{76}{100}$ "
[13]	MI₆ [2560]	262·8	256	255·5	+2·5	$\frac{64}{100}$ "
[14]	Fork [2806]	272·0	266	263·0	−3·0	$\frac{54}{100}$ "

in which N equals the number of vibrations of the lower tone of the interval, and

$$N + \cfrac{1}{\left(\cfrac{42500}{N+23} + 23\right) \cdot 0001}$$

= the number of vibrations of the higher tone of the interval. In column E are given the differences between the computed values [D] and the observed values [C]. The formula gives quite closely the true values from SOL_2 [192 v.d.] to MI_6 [2560 v.d.]. In column F are given the smallest consonant intervals as determined experimentally from SOL_1 [96 v.d.] to the tone of 2806 v.d., expressed in semitones of the equal-tempered scale.

In fig. 11 these intervals, computed from the numbers in column C, are expressed graphically by the curve N.C.I. The units of ordinates (on the left of figure) are semitones, and the units of abscissas are 100 vibrations. This curve shows in a striking manner the contraction of the smallest consonant interval as we ascend the musical scale; while SOL_1 [96 v.d.] requires a sound separated from it by $6\frac{15}{100}$ semitones to give the smallest consonant interval, SOL_6 of 3072 v.d. forms a consonant interval with a higher sound separated from it by only $1\frac{1}{2}$ semitones.

The curve AV, of fig. 11, which has the same units of abscissas as curve N.C.I., and the units of whose ordinates, in number of vibrations, are on the right of the diagram, shows graphically the number of vibrations to be added to the tones, on the axis of abscissas, to obtain the smallest consonant intervals.

The experiments which form the basis of the statements given in Table II., I shall now describe.

Having but few forks below UT_3 in pitch, and those not numerous enough to determine with accuracy the consonant intervals, I requested my friend Dr. Rudolph Kœnig, of Paris, to determine for me the smallest consonant intervals among sounds below UT_3 in pitch. The numbers in the table referring to tones SOL_{-1}, UT_1, SOL_1, UT_2, and SOL_2, experiments nos. 1, 2, 3, 4, and 5 of Table II., were furnished by Dr. Kœnig's experiments. The account of these experiments, which Dr. Kœnig so obligingly made for me, I give in his own words :—

Dr. Kœnig's Experiments.

"Paris, le 21 Mars 1893.

" . . . Je veux maintenant répondre à vos questions concernant la consonance des intervalles formés de notes graves et pas trop fortes, et faire d'abord cette remarque générale, que la perceptibilité des roulements et raucités produits par des battements, qui dépend avant tout de l'intensité relative des deux notes primaires, paraît être presque entièrement indépendant de leur intensité absolue, quand elles sont graves, tandis que le rôle de l'intensité absolue augmente avec leur hauteur.   En effet, les résultats des observations faites avec des diapasons relativement faibles, et sans résonateurs, sont pour les octaves graves presque absolument identiques avec les résultats donnés par les gros diapasons et résonateurs du grand tonomètre, et publiés dans le tableau, page 113, des *Quelques Expériences d'Acoustique*, tandis que pour les intervalles avec les notes fondamentales UT_2 et SOL_2, les différences des résultats devient déjà sensible.   Je pourrais aussi résumer ces faits en disant que l'influence de l'intensité absolue des deux sons primaires sur la perceptibilité de battements, qui est absolument nulle pour les battements lents, augment pour les roulements et raucités avec les nombres des battements qui les produit, car, pour example, les 8 battements de $UT_1 : RE_1$ sont aussi distinctement entendus avec des notes UT_1 et RE_1 très faibles, qu'avec des notes les plus fortes, tandis que le roulement des 32 battements de $UT_1 : SOL_1$, se fait beaucoup plus sentir quand les deux notes sont fortes, que quand elles n'ont qu'une faible intensité.

" Voici maintenant la liste de mes observations :—

" [1] *Intervalles avec la note fondamentale* $SOL_{-1} = 48$ v.d.

" Les diapasons employés, du modèle de l'interrupteur universel, Cat. No. 253, ont des branches d'environ 9 millim. d'épaisseur sur 15 millim. de largeur.

" On ne trouve dans toute l'octave pas un seul intervalle sans battements fortement perceptibles, soit séparément soit comme roulement.   Le roulement paraît le plus faible vers la sixte, $SOL_{-1} : MI_1$.

" [2] *Intervalles avec la note fondamentale* $UT_1 = 64$ v.d.

" Les diapasons employés, du modèle, Cat. No. 234, ont des branches d'environ 10 millim. sur 17 millim.

" Tout se passe dans l'octave entière comme avec les gros diapasons avec résonateurs, seulement le roulement confus près de la quinte est faible et disparaît presque devant les battements secondaires, mais il reparaît au-dessus de $SOL_1 +$ 4 v.d. et devient plus fort en passant au roulement simple des

U 2

battements supérieurs. A la quinte exacte, $UT_1 : SOL_1$, où les battements secondaires manquent, on entend très bien le roulement des 32 battements, mais plus faible qu'avec des gros diapasons et résonateurs.

" Les mêmes expériences répétées avec des diapasons à branches de 19 millim. sur 15 millim. donnent le même résultat.

" En somme, ici aussi il n'y a pas d'intervalle consonant dans toute l'octave.

" J'ai encore particulièrement examiné l'intervalle $UT_1 : MI_1$, mais on y entend le roulement des 16 battements même encore quand les sons primaires sont devenus déjà si faibles qu'on ne les perçoit presque plus.

" [3] *Intervalles avec la note fondamentale* $SOL_1 = 96$ v.d.

" Diapasons employés à branches de 10 millim. sur 17 millim.

" $SOL_1 : LA_1$, 10·6 battements séparément entendus.

„	: SI_1, 24	„	roulement simple fort.
„	: 124 v.d., 28	„	„	plus faible.
„	: UT_2, 32	„	„	très faible.
„	: 134 v.d., ...		faible raucité.

" $SOL_1 : 136 \brace : 138$ Peut-être regardé comme consonant, mais à

" $SOL_1 : 140$ v.d. les battements secondaires deviennent déjà sensibles et augmentent vite en intensité. Quand ils disparaissent à la quinte exacte,

" $SOL_1 : RE_2$, celle-ci fait entendre une raucité à peine perceptible. Au-dessus de RE_2 les battements secondaires reparaissent pour disparaître vers 148 v.d.

" $SOL_1 : 150$ v.d. Il y a encore un peu de raucité mais on pouvait à la rigueur regarder les intervalles d'ici à

" $SOL_1 : 166$ v.d. comme consonants. Au-dessus de 166 v.d. le roulement des battements supérieurs commence, et augmente en intensité, et à partir de 180 v.d. les battements supérieurs sont séparément perceptibles.

" En résumé, il y a entre la quarte et la quinte une petite étendue, et au-dessous et au-dessus de la sixte une plus grande, où se trouvent des intervalles consonants.

" [4] *Intervalles avec la note fondamentale* $UT_2 = 128$ v.d.

" Diapasons employés pour UT_2 jusqu'à UT_3, avec branches de 10 millim. sur 17 millim., pour la note fondamentale UT_2 avec branches de $7\frac{1}{2}$ millim. sur 14 millim.

" Tout se passe à peu près comme avec les gros diapasons et résonateurs (Cat. No. 197), seulement le roulement de $UT_2 : MI_2$ n'est plus qu'un simple raucité, qui diminue vite pour disparaître à 166 v.d.

" UT_2 : FA_2 est consonant, et la consonance persiste jusqu'à 188 v.d. où les battements secondaires commencent à la troubler jusqu'à la quinte, UT_2 : SOL_2, qui est consonant. Quand ils ont troublé la consonance des intervalles au-dessus de la quinte jusque vers UT_2 : 197 v.d. les intervalles sont de nouveau consonants et le restent jusque vers UT_2 : 222 v.d. où alors le roulement des battements supérieurs commence.

" En résumé, les intervalles d'un peu au-dessous de la quarte jusqu'à près de la quinte, la quinte, et les intervalles d'un peu au-dessus de la quinte jusque au-dessus de la sixte sont consonants.

" Avec des diapasons du modèle de Cat. No. 38 a, aux branches de 15 millim. sur 20 millim., montés sur caisses, le roulement des 32 battements de UT_2 : MI_2 est fort ; UT_2 : SOL_2 est consonant, mais comme MI_2 : SOL_2 donne le même nombre, 32, de battements que UT_2 : MI_2, en faisant sonner ensemble UT_2, MI_2, SOL_2, les 32 battements de UT_2 : MI_2 et de MI_2 : SOL_2 se renforcent et produisent un roulement formidable.

" [5] *Intervalle avec la note fondamentale* $SOL_2 = 192$ v.d.

" Diapasons employés avec branches de 10 millim. sur 17 millim.

" SOL_2 : LA_2.　Roulement simple assez fort.
　　　,,　: 244 v.d.　Raucité prononcé.
　　　,,　: SI_2.　Raucité faible.

" La consonance commence encore avant SOL_2 : UT_3.

" Il résulté de l'ensemble de ces observations, que pour les intervalles des notes très graves les faits ne s'accordent pas du tout avec votre loi, mais aussi que pour les intervalles des notes de plus en plus aigues, l'accord entre les faits et la loi devient toujour meilleur et finit par être presque parfait quand la note fondamentale atteint SOL_2."

I experimented on the hearing of twelve persons with all the forks at my command among which I could obtain consonant intervals. It is true that the number of intervals thus furnished, by 80 forks, did not amount to many. Many such intervals can only be obtained in the laboratory of Dr. Kœnig, where is his " grand tonomètre " giving the frequency of all sounds from 16 to 21845 complete vibrations per second. However, I secured, between UT_3 and SOL_6, enough intervals among the forks to establish the law and the facts given in Table II.

All the persons experimented on, except myself and one other observer, were accomplished musicians, several of them

violinists of more than exceptional ability. Three were graduates of the Conservatory of Music of Leipzig.

These experiments were all made in the same manner, viz. by taking the fork giving the lower tone and sounding it successively with others which gave more and more beats per second, till these beats blended into a continuous smooth sensation, forming the smallest consonant interval. As musicians rather avoid than dwell on dissonant intervals, I educated each one in the special subject of the roughness of the sensation given by beats by making the beats more and more frequent till near consonance, then giving an interval which is admitted by every one to be consonant. In this way their hearing was trained in what I wished them to discern, viz. that separation in the pitch of two forks which just gives a consonant interval.

The variation among the decisions of these different observers never equalled two vibrations ; generally they agreed exactly. The agreement among observers in the judgment of a consonant interval is remarkable. I give the mean of these experiments. The number of the paragraphs refer to the number of the experiment given in Table II. :—

[6] $UT_3 : MI_3 = 256 : 320$ gave a consonant interval. I narrowed the interval by lowering the pitch of MI_3 from 320 to 315, 314, 313·5, and 313.

$UT_3 : 315$ consonant.

„ : 314 just consonant.

„ : 313·5 slightly rough.

„ : 313 decidedly rough.

These experiments show that $256 : 256 + 58 =$ smallest consonant interval.

[7] $MI_3 : SOL_3 = 320 : 384$ is decidedly rough. Separated the interval by lowering the MI_3 fork from 320 to 316; then

$MI_3 : SOL_3 = 316 : 384 = 316 : 316 + 68 =$ smallest consonant interval.

[8] $LA_3 : UT_4 = 439 : 517·4$ decidedly harsh. Separated interval by lowering LA_3 of 439 v.d. to 432 v.d. ; then

$LA_3 : UT_4 = 432 : 517·4 = 432 : 432 + 85·4 =$ smallest consonant interval.

[9] $RE_4 : FA_4 = 576 : 682·65$ slightly rough. Increased the interval by lowering RE_4 of 576 v.d. to 575 v.d.; then

$RE_4 : FA_4 = 575 : 682·65 = 575 : 575 + 107·65 =$ smallest consonant interval.

[10] $SOL_4 :$ fork of 896 v.d. $= 768 : 896$ slightly rough. Increased the interval by lowering SOL_4 of 768 v.d. to 766·2; then

$SOL_4 : 896 = 766.2 : 896 = 766.2 : 766.2 + 129.8 = $ smallest consonant interval.

[11] $LA_5 : SI_5 = 1706.6 : 1920$ consonant. Narrowed the interval by lowering SI_5 of 1920 to 1917; then

$LA_5 : SI_5 = 1706.6 : 1917 = 1706.6 : 1706.6 + 210.4 = $ smallest consonant interval.

[12] $RE_6 : MI_6 = 2304 : 2560$ consonant. Narrowed the interval by lowering MI_6 of 2560 v.d. to 2549; then

$RE_6 : MI_6 = 2304 : 2549 = 2304 : 2304 + 245 = $ smallest consonant interval.

[13] MI_6 : Fork No. $11_6 = 2560 : 2816 = 2560 : 2560 + 256$ is just perceptibly rough.

[14] Fork 11 : $SOL_6 = 2816 : 3072$ slightly dissonant. Increased interval by lowering Fork 11 of 2816 v.d. to 2806; then

Fork $11 : SOL_6 = 2806 : 3072 = 2806 : 2806 + 266 = $ smallest consonant interval.

In the experiments just described the intervals of the tones that gave consonance were made by simple tones of small intensity and without the slightest trace of the upper partial tones of the forks, and the two forks were vibrated so that they gave, as near as I could judge, the same intensity of sound. The results given only refer to intervals so formed. To obtain them the forks were gently vibrated by strokes of rubber hammers that varied in hardness with the pitch of the forks. The lower the pitch of the fork, the softer should be the hammer. A hammer of hard rubber striking low-pitched forks will develop the upper partial tones of the forks, and so vitiate the experiments that a really consonant interval might be judged as dissonant.

The results of all the experiments may be summed up as follows :—From SOL_2 of 192 v.d. to MI_6 of 2560 v.d. the smallest consonant intervals are closely given by the formula

$$N : N + \frac{1}{\left(\dfrac{42500}{N+23} + 23\right).0001}.$$

For sounds below SOL_2 the interval as computed by the formula is too small to agree with the true interval. For sounds above MI_6 (2560 v.d.) the intervals computed by the formula, like those below SOL_2, are too small. That the experimental determination of the smallest consonant intervals throughout four octaves, upward from SOL_2, or throughout the tones given by the violin, should agree so closely with the formula indicates the existence of a law connecting the mag-

nitude of the smallest consonant interval with its position in the musical scale.

Dr. Kœnig has shown that a consonant interval does not exist among simple sounds of pitch below SOL_1 [96 v.d.], yet I have found that the sound of UT_1 [64 v.d.], when interrupted by a rotating perforated disk, blends perfectly, to my ear, when these interruptions occur 23·1 times in a second. It may appear strange that although 23·1 interruptions per second of the sound UT_1 blend, yet a consonant interval does not exist throughout the octave of UT_1 till the interval of $UT_1 : UT_2$ is reached ; but the beats produced by the rotating perforated disks are produced by the interruptions of one tone, whereas when two simple tones are conjoined two sets of beats are produced, inferior and superior : thus, when UT_1 forms an interval with $UT_1 + 23$ v.d., the inferior beats are 23 per second and the superior beats are 41 per second, and the interaction of these inferior and superior beats produces secondary beats, which give to the interval a confused rumbling sound *. Of this interval $UT_1 :$ $UT_1 + 23\cdot1$, Dr. Kœnig wrote to me as follows :—" Your 23·1 interruptions of UT_1 correspond, in number, to the inferior beats of the interval of the simple tones $UT_1 : UT_1$ $+ 23\cdot1$, but it is just at this magnitude of interval that the superior beats begin to assert themselves, to produce with what remains perceptible of the inferior beats the confused rumbling, which evidently would be but a slight roughness (disappearing entirely at a further increase of the interval), if the superior beats, whose intensity from this point increases with the interval, did not exist."

3. *The Durations of the Residual Sonorous Sensations as deduced from the Smallest Consonant Intervals among Simple Tones.*

If we assume that two simple tones form the smallest consonant interval because the beats produced by these conjoined sounds have blended into a smooth continuous sensation, then we may deduce the durations of the residual sonorous sensations from the observed smallest consonant intervals in the following manner :—The reciprocals of the numbers in column C of Table II. are taken as expressing the durations of the sonorous sensations given by tones whose numbers of vibrations are the mean of those of the lower and higher tones of the corresponding consonant intervals, for,

* See *Quelques Expériences d'Acoustique*, par Rudolph Kœnig (Paris, 1882), pp. 89, 107, 113.

when two sounds of different pitch blend, there is no reason why the duration of their residual sensation, as given by the reciprocal in column C, should refer to the lower sound more than to the higher.   Therefore we have taken these reciprocals from column C as expressing the durations of sounds having the mean pitch of the two associated sounds forming the interval.   The residual sensations thus found were projected in a curve, drawn to a large scale.   From this curve were obtained the durations of the residual sonorous sensations of the tones of the musical scale.   These durations are given in column H of Table I.

In column I of Table I. are given these durations as computed by the formula

$$D = \left(\frac{48{,}000}{N + 30} + 21\right) \cdot 0001.$$

In column K are given the differences between the durations computed by the formula and the durations given in column H.   The differences show that the formula expresses closely the durations of the residual sensations thus deduced from the determinations of the smallest consonant intervals, except in the case of UT_2; for which tone the computed number of vibrations to be added to it to form the higher tone of its smallest consonant interval, as shown in Table II., is 5·2 vibrations less than the number really required.

In fig. 11 these durations, as determined from the smallest consonant intervals, are plotted in the curve F, so that the comparison of the durations of the residual sonorous sensations thus determined may be readily compared with those given (by the curve I) of the residual sensations as determined by the blending of sounds interrupted by rotating perforated disks.

The ordinates of the curves I and F of fig. 11 are obtained in fractions of a second by changing the numbers 1, 2, and 3 on the left of fig. 11 into ·01, ·02, and ·03.

These two curves of fig. 11 present the same general character of a rapid upward flexure at the points corresponding to the pitch of about 600 v.d.

The durations of the sound-sensations as deduced from the smallest consonant intervals of the forks average about $\frac{1}{3}$ greater than those given by the beats of interrupted sounds. It may be supposed that the durations of the sonorous sensations deduced from the smallest consonant intervals of simple tones are greater than those determined by sounds interrupted by the perforated disks, because in the resultant actions of the vibrations of the tones, forming the smallest

consonant intervals, the periods of silence, or the periods of great diminution of sound, are a fraction of the periods of sound, or of the periods of maximum intensity of sound. To test this opinion I combined the sinusoids corresponding to the two tones of various smallest consonant intervals. On taking as the residual duration of the sound, not the time from maximum to maximum of vibration (as in the deduction of the durations from the smallest consonant intervals), but the interval of time during which much diminished intensity of sound exists, as shown in the combined curves, I found that the durations of the sonorous sensations were thus reduced, on the average, about $\frac{1}{2}$, whereas the reduction in time should be only $\frac{1}{3}$ to make these durations agree with those determined by the rotating perforated disks. The explanation suggested is therefore not tenable.

For the period of much diminished intensity of sound I took that length (in time) of the resultant curve which is bounded, at each end, by an amplitude of vibration $\frac{1}{2}$ of the maxima amplitudes of the curve. We here are in doubt as to the relative intensities of the sensations given by two sound-vibrations whose amplitudes are 2 : 1, and whose energies are as 4 : 1. We at once face an obstacle which, from our want of knowledge, is insurmountable: for, assuming that either the law of Weber, or the formula of Fechner deduced from it, correctly gives the relations existing between the intensity of a stimulus and its corresponding sensation, we cannot apply either of these laws, because we do not know the *absolute energies* of the sound-vibrations whose sensations are to be compared. Thus, if we adopt the law of Weber, with the least perceptible difference in the sensation of two sounds equal to $\frac{1}{3}$ of their energy, as given by the experiments of Volkmann *, we find that if 1 and 4

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* In the investigations on this subject of which I have knowledge, the experimenters have used either noises, or sounds of complex composition mingled with noise, and the ways in which they have determined the relative energies of sounds, or noise-producing vibrations, are open to criticism. I do not know of similar experiments made with simple sounds or tones. I would suggest that the problem of determining the difference in the energies of two simple sounds to give a perceptible difference in the sensations they cause may be solved as follows:—A fork or rod is vibrated with a constant amplitude, and this amplitude is accurately measured with a micrometer-microscope. A second fork, or rod, placed alongside of the first fork or rod, has a much smaller amplitude of vibration, which can be varied, and is also measured with a microscope. The second fork differs from the first slightly in pitch, so that, say, three beats per second are given. The amplitude of the second, or of the first fork, is varied till the perception of beats just vanishes, or just appears, while the ear is kept at a fixed distance from the forks.

are the absolute energies of the sound-vibrations, we get for the ratio of their corresponding intensities of sensations 1 : 2·6 ; but if the absolute energies of the sounds are 10 and 40 (and their ratio is also 1 : 4), we get for their relative sensations 1 : 1·48.   Or, what is the same, on the curve expressing the law of Weber, or of Fechner, the ratio of the sensations of two sounds as given by their corresponding ordinates depends on the number of units in the abscissas forming the ratio of the energies of these sounds.

Professors Cattell and Fullerton, from extended experiments " On the Perception of Small Differences " *, very carefully made and skilfully reduced, have formed the opinion that neither the law of Weber nor Fechner's formula is correct, and *à priori* considerations lead them to the opinion that it is probable that the sensation is directly as the stimulus. If the sensation increases directly as the stimulus, then we can obtain the relative sensations of two sounds whose relative energies are known.   Adopting this relation, we have 1 : 4 as the ratio of the maximum sensation in the periods taken

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If we take for the relative intensities of the sound-giving vibrations the ratio of the squares of the amplitudes of the forks, the least perceptible difference in sensation corresponding to the differences in the energies of the sounds may be computed.   As example, suppose the second fork has $\frac{1}{20}$ of the amplitude of vibration of the first.   Then the energy of the maximum sounds of the beats will be $\overline{20+1}^2=441$, and the energy of the minimum sound of the beating will be $\overline{20-1}^2=361$, and $\frac{441}{361}=$ the ratio of the stimuli giving the least perceptible difference in sensation.   Sound-vibrations of different amplitudes and of different pitch will have to be experimented with, and the fork giving the greater amplitude of vibration should, in successive experiments, be lower in pitch, and then higher in pitch, than the fork giving the lesser amplitude of vibration, for reasons set forth in my research (1) " On the Obliteration of the Sensation of one Sound by the simultaneous action on the ear of another more intense and lower sound; (2) On the Discovery of the Fact that a Sound even when intense cannot obliterate the sensation of another Sound lower than it in pitch " (Phil. Mag. Dec. 1876 ; 'Nature,' Aug. 10, 1876).   Such a research will be difficult and tedious, and will require many precautions in arranging the experiments.

Any one may readily observe the phenomena described by sounding a fork with long amplitude of vibration, and, gradually bringing up to the ear a second fork with a small amplitude of vibration, giving with the first three beats per second.   As the latter fork gradually approaches the ear the beats become stronger, reaching a maximum of intensity, and then diminishing till, at a certain distance of the fork from the ear, they vanish in the more intense sensation of the more intense sound, to reappear when the faintly vibrating fork has been brought closer to the ear.

* 'Publications of the University of Pennsylvania,' Philosophical Series, No. 2, May 1892,

for those of much diminished sound to the maximum sensation in the periods of much increased sound, as given by the measurements of the amplitudes of the resultant curves of the smallest consonant intervals.

In explanation of the facts and laws given in this paper I have no hypothesis to offer. It appears to me that the present condition of our knowledge of audition demands that we should ascertain more facts relating to it before we frame hypotheses on the mechanism and action of the apparatus of hearing.

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XXIV. *A Study of the Polarization upon a Thin Metal Partition in a Voltameter.*—Part II. *By* John Daniel. [*]

IN this paper two questions will be discussed : first, the passage of ions through a gold-leaf partition in a voltameter ; second, the minimum current-strength at which the ions are deposited visibly upon the partition for various electrolytes. This will be called the " critical current." This paper is a continuation of the work done last spring in Berlin in the quantitative measurement of the polarization upon metal partitions ranging in thickness from ·0001 millim. to ·02 millim. for various current-strengths in a 30-per-cent. H_2SO_4 voltameter. In those experiments there was no development of gas nor polarization on a gold-leaf partition (·0001 millim. thick) for the highest current used, which was four tenths to five tenths ampere.

The present apparatus consists *essentially* of a glass voltameter vessel with platinum electrodes separated by the metal partition under investigation, so that there is no path for the current except through this partition ; an accurate current-measurer, and a strong, steady battery. The voltameter consists of an outer glass jar 8 centim. high, 8 centim. wide, and 8 centim. long ; and a glass jar 8 centim. high, 5 centim. wide, and 5 centim. long, placed inside the first jar. A platinum kathode suspended by a platinum wire is placed inside the inner jar, and a similar electrode serves as anode in the larger jar, though a copper anode was sometimes used when the electrolyte was $CuSO_4$. A hole 2 centim. in diameter was bored in one side of the smaller jar. Glass

plates 4 centim. wide, 6 centim. long, and 1 millim. thick were bored with a hole 1·5 centim. in diameter. Powdered sealing-wax was placed around the edge of this hole, melted, and the gold-leaf secured to the melted sealing-wax.

This plate was then securely and perfectly (*i. e.* with no possible chance for leakage) sealed upon the side of the inner jar so that the gold-leaf was over the hole almost centrally. The voltameter was then carefully filled, keeping the liquid inside and outside on the same level so as not to break the gold-leaf partition, and was then ready for use.

To measure the current, a Thomson No. VI. Composite Electric Balance (No. 106), and a Weston double-scale ammeter No. 598, ranging from 0 to 1·5, reading directly to ·01 ampere and estimated to ·001, and from 0 to 150, reading to amperes and estimated to ·01, were used in series with the voltameter. The two instruments were found to agree so well that the Weston ammeter was used alone for most of this work as it was much more convenient to read.

The battery consisted of 25 Accumulator Company " 23 M " type accumulators, 350 ampere-hours capacity, 50 volts E.M.F. The current-strength was adjusted to any desired value by resistance in series, which could be varied at pleasure between zero and 12,000 ohms. For sealing-wax, pure rosin and bees-wax (without colouring-matter), mixed in such proportion as to give a low melting-point, was used. The gold-leaf used was bought in Nashville, and is known to the trade as " XX." It is about ·0001 millim thick.

Careful selection was made of such parts of the gold-leaf as were found, by holding up to the light, to be free from small holes. It has already been observed, in Part I. of this paper, that when $CuSO_4$ was used as the electrolyte and the current-strength was *over* ·3 *ampere*, Cu was deposited on the rim of the gold-leaf, which was necessarily larger than the hole in the glass plate. In this work it was found necessary to remove this gold quite close up to the edge of the hole by scraping it off, as was first tried, or by covering it carefully with sealing-wax, which was found both easier and better. This was accomplished by melting the sealing-wax over the gold with a hot brass hammer of peculiar shape made for the purpose. The wax could thus be made to flow quite close to the edge of the hole. This left only that part of the gold exposed which was immediately over the hole. To neglect this was in all cases to reduce the critical current, the deposit of the cation appearing first on that part of the gold-leaf which was nearest the anode and farthest from the opening.

Passage of the Ions through the Gold-leaf Partition.

To test this, $CuSO_4$ solution (17 per cent. *i. e.* 1 gram $CuSO_4$ to 5 cub. centim. H_2O) was used in the outside vessel (anode side of the voltameter), and H_2SO_4 (30 per cent. solution, sp. gr. 1·23) in the inside vessel (kathode side of the voltameter). These solutions being separated by the gold-leaf partition, the appearance of the ions upon the electrodes and upon the partition, when the current was closed, was noted. The first method of observation was to close the circuit upon the voltameter, read the current-strength by the ammeter, and at stated intervals weigh the Cu deposited on the kathode. This gave Table I., where it may be seen that the amount of Cu deposited was very small at first, not more than 2 per cent. or 3 per cent. the first hour, but increased rapidly with the time.

This did not settle the question as to whether the current caused the copper to pass through the gold-leaf partition or not.

The second method was to set up two exactly similar voltameters at the same time, close the circuit on one leaving the other open, and at stated intervals weigh the Cu deposited on the kathode of the voltameter through which the current had passed, and at the same time make a quantitative analysis of the solution on the kathode side of both the open and the closed voltameters. This was done by extracting 10 cub. centim. from each with a pipette, and depositing the Cu electrolytically in two similar platinum crucibles connected in series. Equilibrium was maintained in the voltameter by adding 10 cub. centim. of the 30 per cent. H_2SO_4 solution to replace the 10 cub. centim. thus removed. Knowing the volume of solution in each voltameter, these analyses were sufficient to determine the total amount of Cu that had passed through the partition during the same interval for each voltameter. Table II. gives the results.

Here it was observed that imperceptible differences in the specimens of gold-leaf were sufficient to cause enough difference in the diffusion to leave the question unsettled. The amount passing the partition of the open voltameter was as often *greater* as it was *less* than that of the closed voltameter. It was now evidently necessary to test one and the same gold-leaf partition for diffusion with circuit open and closed successively. This leads to the third method shown in Table III.

It is thought that this is entirely free from objection or serious error, and leads to the conclusion that the current does not sensibly affect the diffusion of $CuSO_4$ and H_2SO_4

through the gold-leaf partition. This method, in detail, was to set up two similar voltameters at the same time, leaving both open, and making quantitative analyses at stated intervals; then, closing the current on both in series, to again make quantitative analyses of the solution on the kathode side and weigh the Cu on the kathodes: finally to break the circuit and again repeat the analyses.

Curves plotted from these results show *no break nor change of slope* for the intervals during which the current was passing. In the foregoing experiments there was no deposit of Cu on the gold-leaf partition provided the current was less than about 0·3 of an ampere. The time-curves for the two specimens of gold-leaf are not identical, showing a different rate of diffusion, but are quite similar in shape.

Using a Cu anode there was no visible gas on the anode, but the anode was dissolved by the current in the usual manner. Using a platinum kathode and a platinum anode, there was, of course, an escape of gas from the anode proportional to the current-strength.

Gas always escaped from the Pt kathode, proportionally but less as the amount of Cu deposited increased. In the case where the *partition* was *removed* and the solutions thoroughly mixed there was no gas, but the full amount of Cu deposited on the kathode.

Thus it seems that the passage of the current in such a voltameter is not accomplished by the passage of the Cu through the gold-leaf partition. Some of the $CuSO_4$ passes the partition by *diffusion*, and then does its proportional part of the conduction of the mixed solution of $CuSO_4$ and H_2SO_4, which accounts for the increased *percentage* of Cu deposited on the kathode as the interval from the time the voltameter was filled increases.

In the time-curves which may be constructed from Table III. (Pl. IV. fig. 2) it will be noticed that the amount of Cu at the end of the first interval seems too small, causing a similar bend in both curves. This is doubtless due to the fact that the current was not continued long enough to deposit all the Cu in the 10 cub. cent. sample. The amount of $CuSO_4$ present being very small, it would be deposited very slowly; and the circuit should have remained closed several hours instead of less than an hour, as was the case. A *similar* bend occurs in both curves, because the specimens were analysed in series and the same defect applies to both alike. If the current was increased beyond about 0·3 ampere, with $CuSO_4$ and H_2SO_4 as the solutions, separated by a gold-leaf partition, there was development of gas and Cu on the partition. This

brings us to the second problem, *i. e.*:—The minimum current-strength at which the ions are deposited visibly on the gold-leaf partition for various electrolytes.

Critical Current-Density for Gold-leaf.

This part of the investigation consists simply in closing the circuit on the voltameter with a high auxiliary resistance, gradually and slowly increasing the current by decreasing the resistance, and observing at what current-strength bubbles of gas or deposit of metal *begin* to appear upon the partition. Table IV. shows these values for various solutions used as electrolytes, with a gold-leaf partition. Table V. gives the results in 30 per cent. H_2SO_4 for aluminium-leaf, platinum-leaf, and gold-leaf respectively.

Table V. shows the same for a gold-leaf partition in H_2SO_4 of various concentrations from 100 per cent. (?) to 0·5 per cent.

Unfortunately, the importance of the concentration of the solution in affecting the value of the " critical current " was not noted until after several of the solutions had been tested and thrown away without measuring their concentration or specific gravity, which is therefore not given for those cases. The specific gravity of those solutions for which it *is* given was determined by a very sensitive and accurate set of hydrometers reading directly to 0·001. Table V. gives the case of 30 per cent. H_2SO_4 with Pt partitions of various thicknesses ; also of a "thick" Pt partition perforated with 1, 2, 3, and 4 holes successively, each 0·5 millim. in diameter. This is important as showing that the very small holes which may have existed in the carefully selected gold leaves used as partitions could not have had much, if even a sensible, influence on the value of the critical current.

Table VI. shows the interesting case of a 0·02 millim. palladium partition in 30 per cent. H_2SO_4.

The values given in the Tables are in most cases the mean of several determinations which differed but slightly.

The importance of having the edges of the partition covered well up to the edge of the hole in the glass was emphasized in this work on account of the fact that the anode was usually placed on one side, and sometimes even at the back of the inner vessel, instead of in front, in order not to obscure a free inspection of the partition, and to avoid the disturbance of the gas escaping from the anode, as this was considerable with the strongest currents used, *i. e.* ten to twelve amperes. Thus one edge of the exposed partition being nearer to the anode than the opening, the deposit would always begin first on the nearest edge.

Inspection of the Tables will show that in 30 per cent. H_2SO_4 the gold-leaf partition will pass about ten amperes before gases are developed upon it. Platinum-leaf and aluminium-leaf showed sensibly the same "critical current," rather less for the aluminium, which was, however, thicker though not so free from holes.

A solution of CdI_2 showed regular deposit of both Cd and I upon the partition for the weakest current to 0·001 ampere. This case was peculiar in having both ions *solids* and indicated as a consequence that neither would pass through the gold-leaf partition.

Using 9 per cent. $AgNO_3$ solution, Ag_2O_2 was deposited on the anode, but this came about by secondary action at the anode; and though we have in this case also two solids deposited on the electrodes as the result of the electrolysis, one of them is not primarily a solid, and the critical current is of the order of magnitude of that for other metallic salts. A similar case was found in that of $MnSO_4$ solution, where MnO_2 was deposited on the anode.

A solution of lead acetate gave PbO_2 on the anode, but showed a very low "critical current."

An interesting fact is the dependence of the "critical current" upon the concentration of the electrolyte, as shown in Table V., indicating that the "critical current" is proportional to the conductivity of the electrolyte. I have made some experiments to determine whether variation of the temperature has the same effect upon the "critical current" as upon the conductivity, though the results are as yet hardly sufficient to justify a conclusion. I have been entirely unable anywhere to get a series of platinum partitions of thicknesses suitable to repeat the quantitative measurements of polarization which were made in Berlin for the gold plates. Table VI. for 0·02 millim. palladium is interesting. Either gold, platinum, or aluminium as thick as this behaves like a very thick plate, *i. e.* shows gas at once in amount corresponding to the current-strength. When first set up, the 0·02 millim. palladium partition showed a "critical current" of 0·08 ampere. After considerable use the "critical current" has gradually, though not slowly, increased to 0·3 in 30 per cent. H_2SO_4. This seems to be quite distinct from the well-known property of palladium of occluding gases, especially H; for this plate will pass 0·2 ampere or more for hours without showing gas, and develops gas *at once* for a little stronger current. The gas on the partition of palladium will cease to escape if the current be *again reduced* below the "critical" value. Currents of several amperes have several times been passed

through this partition, developing profuse gas, and it was thought probable that the palladium was being dissolved by the 30 per cent. H_2SO_4 under the action of the current. Accordingly a test of the solution was made for palladium by adding ammonia till alkaline, and then adding ammonium sulphide, which gave no indication of the presence of palladium.

It has been observed that Pt is perfectly constant, showing the same "critical current" as often as tested. Gold is oxidized the first time the "critical current" is attained, and its value decreases on repeating the test (with the same specimen).

Efforts were made to test the critical currents for four thicknesses of gold from 0·0004 to 0·0018 millim., in ammonium nitrate, hoping that this would not oxidize the gold; but the partitions were oxidized by currents strong enough to develop gas.

Table I.

A 17 per cent. solution of $CuSO_4$ with a Cu anode, separated by a gold-leaf partition from a 30 per cent. solution of H_2SO_4 with Pt kathode.

Time, in minutes.	Current, in amperes.	Cu deposited on kathode, in grms.	Ratio of Cu to current.
30	0·175	0·003	3 per cent.

Allowed this voltameter to stand from Saturday till Monday, and then made the following determinations in rapid succession :—

Time, in minutes.	Current, in amperes.	Cu deposited on kathode, in grms.	Ratio of Cu to current.
33	0·205	0·0765	38 per cent.
40	0·206	0·0920	57 ,,
40	0·127	0·0700	70 ,,
45	0·054	0·0380	80 ,,

Set up two new voltameters, #1 and #2, and connected them in series. The gold-leaf partition in #2 broke before the current was closed. Then the following values were found :—

		#1.	#2.	#1.	#2.
30	0·132	0·002	0·0766	2·6 p. c.	99 p. c.

Then after standing some hours,

		#1.	#2.	#1.	#2.
30	0·147	0·027	0·085	31 ,,	99 ,,
32	0·152	0·0453	0·095	47·6 ,,	100 ,,

Fresh solutions. Partition of #1 is single gold-leaf; of #2 is double gold-leaf. Then :—

		#1.	#2.	#1.	#2.
65	0·035	0·0022	0·0026	5 p. c.	5·7 p. c.

TABLE II.

To test diffusion of 17 per cent. $CuSO_4$ and 30 per cent. H_2SO_4, with current passing in voltameter #1 and no current passing in #2.

Time, in min.	Current, in amperes.		Cu on kathode.		Percentage of Cu to current.		Cu in 10 c.c. solution.		Total Cu passed the gold.	
	#1.	#2.	#1.	#2.	#1.	#2.	#1.	#2.	1#.	#2.
92	·0505	0·0	·0058	0·0	6·4	0·0	·002	·0023	·0308	·0300
87	·053	0·0	·0143	0·0	15·8	0·0	·004	·005	·0643	·0650
Fresh solutions and single gold-leaf partitions.										
45	·15	0·0	·0022	0·0	1·7	0·0	·0043	·0040	·055	·048
65	broke	0·0	......	0·0	......	0·0	......	·006	......	·076
18 hrs.	......	0·0	......	0·0	......	0 0	......	·0256	......	·3172
Fresh solutions and gold-leaf partitions.										
55	·077	0·0	·0022	0·0	5·3	0·0	·0014	·0033	·019	·041
60	·077	0·0	·0090	0·0	20·0	0·0	·0035	·0065	·034	·085
60	·079	0·0	·0142	0·0	30·8	0·0	·0038	·0084	·0797	·1148
Began the above at $12^h 55^m 30^s$: closed at $3^h 30^m 30^s$.										

TABLE III.

Third and best Method.

Fresh Solutions and Gold-leaf Partitions,

Time, in min.	Current, in amperes.		Cu on kathode.		Percentage of Cu to current.		Cu in 10 c.c. solution (in grains).		Total Cu passed the gold.	
	#1.	#2.	#1.	#2.	#1.	#2.	#1.	#2.	#1.	#2.
60	0·0	0·0	0·0	0·0	0·0	0·0	·0019	·0006	·0228	·0075
60	0·0	0·0	0·0	0·0	0·0	0 0	·0055	·0024	·0679	·0306
Then the circuit was closed.										
45	·10	·10	·0154	·0060	35	13·7	·0074	·0036	·1116	·0340
45	·10	·10	·0205	·0100	47	22·8	·0080	·0038	·1467	·0701
Again leaving the circuit open, the following was obtained :—										
60	0·0	0·0	0·0	0·0	0·0	0·0	·0090	·0048	·1667	·0864
16 hrs.	0·0	0·0	0·0	0·0	0·0	0·0	·0310	·0187	·5387	·3200

TABLE IV.

Showing the minimum current at which the gases developed visibly upon a *gold-leaf* partition in various electrolytes. The electrodes were platinum. The values given are usually the mean of several determinations.

Electrolyte.	Sp. gr.	Current.	Current-density.	
$CuSO_4$	17 p. c.	0·17	0·10	
$AgNO_3$	9 p. c.	0·40	0·23	Ag_2O_2 formed on anode.
CdI_2	5 p. c.	The feeblest current.	Less than ·001.	
Lead acetate ...	1·10	0·018	0·01	PbO_2 on anode.
$ZnSO_4$	Saturated.	0·19	0·11	
$MnSO_4$	...	0·15	0·08	MnO_2 on anode.
$FeSO_4$	1·10	0·32	0·18	
$SnSO_4$	...	0·30	0·17	
$NiSO_4$	...	0·13	0·07	
Sul. Am. & Fe	...	0·18	0·10	
Sul. Am. & Ni	...	0·31	0·18	
$HgSO_4$	...	0·17	0·10	
Am. nitrate ...	1·05	0·65	0·37	
,, ,, ...	1·10	2·80	1·60	
,, ,, ...	1·135	3·00	1·75	
Am. acetate ...	1·06	1·10	0·63	
,, ,, ...	1·09	0·70	0·40	
Na acetate ...	Saturated.	0·75	0·43	
Na benzoate ...	...	0·75	0·43	

A 96 per cent. solution of acetic acid was found to have too high a resistance to give a sensible current with 50 volts E.M.F. Benzoic acid dissolved in the same was also an insulator.

TABLE V.

The Critical Current in 30 per cent. H_2SO_4 for Aluminium-leaf, Platinum-leaf, and Gold-leaf:—

Partition.	Critical current.	Current-density.
Al	8·0	4·57
Pt	10·0	5·71
Au	10·0	5·71

Table V. (*continued*).

Influence of concentration upon the value of the Critical Current, using a Gold-leaf partition :—

Electrolyte.	Concentration.	Current.	Current-density.
H_2SO_4.........	100 per. cent. ?	0·55	0·31
,, ...	55 ,,	4·5	2·57
,, ...	43 ,,	8·0	4·57
,, ...	30 ,,	10·0	5·71
,, ...	22 ,,	8·0	4·57
,, ...	15 ,,	6·0	3·43
,, ...	4 ,,	1·8	1·03
,, ...	0·5 ,,	0·23	0·13

Using a 30 per cent. solution of H_2SO_4, Pt partitions were used and gave the following values for the Critical Current :—

Pt partition.	Current.	Current-density.
0·00333	0·090	0·051
0·0050	0·002	0·0011
0·02	Weakest current.	

To test the influence of very small holes in the specimens used as partitions, the 0·02 millim. Pt partition was punctured successively with 1, 2, 3, and 4 holes, each 0·5 millim. in diameter. This gave the following values for its Critical Current :—

Partition.	Current.	Current-density.
One hole	0·07	0·04
Two holes	0·13	0·07
Three ,, ...	0·20	0·115
Four ,, ...	0·27	0·154

Table VI.

Showing the increasing Critical Current of 0·02 millim. Palladium in a 30 per cent. solution of H_2SO_4.

Date.	Current.	Current-density.	
Jan. 31	0·08	0·045	
„ „	0·10	0·057	
Feb. 4	0·15	0·086	After much use.
„ 8	0·17	0·10	
„ 17	0·25	0·14	
„ „	0·26	0·15	
„ 18	0·27	0 154	
„ „	0·27	0·154	

A new specimen of the same palladium is being tested and is showing the same phenomenon of increase of the critical current. This last specimen was carefully selected and has *no* holes. Its critical current at first was 0·016 ; after some use it is now 0·043.

I have begun to use a solution of sodium acetate with the hope that it will not oxidize the gold. I can already say that it is at least very much less active than sulphuric acid ; it also shows a decided *temperature coefficient* for the critical current. This part of the investigation will be resumed when opportunity offers.

Vanderbilt University, Nashville, Tennessee,
        February 22, 1893.

Note added April 15, 1893.

More satisfactory specimens of palladium have not yet been obtained, so the matter is left for the present with the seemingly anomalous results recorded above as I find in my note-book.

As regards the temperature coefficient of the " critical current-density," I requested Mr. R. W. Clawson, a student in the laboratory, to make some measurements which are tabulated below.

It may be well to state that the method of observation, that of observing the first appearance of *visible* gas, is not very sensitive, because this development of gas on thin partitions is not quite sudden and sharply defined, but begins gradually, especially with very thin partitions. The probable error of

a reading is, however, not more than 5 per cent., I think. Only "XX" gold-leaf has been used in a solution of sodium acetate. The method was to set up the voltameter with gold-leaf partition, close the circuit, and run the current up till the "critical current-density" was reached. Current and temperature were recorded, the current slightly reduced and allowed to pass till the temperature had risen, say 5 degrees, when the current was again increased to the "critical" value for this new temperature. The limit was reached at about 45 degrees C., when the sealing-wax softened. Since both "critical current-density" and *conductivity* of the electrolyte increase with temperature, effort was made to learn whether both these quantities have the same temperature coefficient by raising the current just to the critical value, and without altering the outside resistance to observe if the increasing current, due to increasing conductivity of the electrolyte, just sufficed to maintain an incipient escape of gas at the partition. In every case the gas soon ceased to escape on being left alone after adjusting the current to a given temperature, requiring always some reduction of the outside resistance to regain the critical current for the higher temperature. A quantitative correction for the temperature coefficient of the outside metallic resistance in the circuit would probably account for the discrepancy.

Table VII.

Temperature Coefficient of Critical Current.

Sodium Acetate ; sp. gr.＝1·06.   Gold-leaf partition.

Temperature......... 22° 24° 26° 29° 30° 33° 35°
Current.............. ·65 ·70 ·76 ·80 ·85 ·92 ·96

Temperature......... 24° 27°
Current.............. ·53 ·64

New partition.

Temperature......... 24° 26°
Current.............. ·54 ·60

New partition.

Temperature......... 22° 23° 24°
Current.............. ·53 ·57 ·59

New partition.

Temperature......... 24° 33° 41° 45°
Current.............. ·77 1·18 1·33 1·48

New partition.

Temperature......... 15° 17° 19° 20° 23° 26° 30° 33° 37° 40°
Current.............. ·30 ·37 ·45 ·50 ·65 ·74 ·83 ·96 1·92 1·15

Table VII. (*continued*).

New solution Sodium Acetate ; sp. gr.=1·13.

Temperature	23°	27°
Current	·70	·80

New partition.

Temperature	23°	28°
Current	·80	1·0

New partition.

Temperature	24°	30°	35°	38°
Current	·95	1·05	1·20	1·29

New partition.

Temperature	14°	19°	24°	29°	34°	39°	44°
Current	·57	·67	·78	·85	·93	·98	1·05

New partition.

Temperature	30°	36°	41°	46°
Current	·87	·91	·99	1·1

New partition.

Temperature	25°	30°	35°	40°
Current	·71	·76	·86	·94

Same partition.

Temperature	25°	30°	35°	40°	45°
Current	·60	·65	·69	·74	·82

New specimen.

Temperature	25°	30°	35°	40°	45°
Current	·72	·85	·92	·98	1·05

Same gold-leaf, repeated.

Temperature	25°	30°	35°	40°	45°
Current	·72	·85	·92	·98	1·05

The means of all the above results plotted give almost a straight line (Plate IV. fig. 3).

XXV. *Calculation of the Coefficient of Self-Induction of a Circular Current of given Aperture and Cross-Section.* By Professor G. M. MINCHIN, *M.A.*[*]

LET ACB (fig. 1) represent a circular wire in which a current of strength i is circulating ; let O be its centre and OV its axis (perpendicular to its plane); let P be any point in space and through P describe a circle, PQ, parallel to the plane of the current, its centre being V on the axis. It is required to calculate the normal flux of magnetic force passing through the circle PQ. If $VP=x$, and the vector potential of the current at P is G (this latter being, of course,

perpendicular to VP and parallel to the plane of the current), the component, Z, of the magnetic force at P parallel to OV is given by the expression

$$Z = \frac{dG}{dx} + \frac{G}{x}. \quad \ldots \ldots \quad (1)$$

(See my paper on the "Magnetic Field of a Circular Current," Phil. Mag. April 1893). This can be written

$$Z = \frac{1}{x} \frac{d(Gx)}{dx}. \quad \ldots \ldots \quad (2)$$

The function G.x is the same as Stokes's *current function* which exists for fluid motion which is symmetrical about an axis. (See Basset's 'Hydrodynamics,' vol. i. p. 12.)

Fig. 1.
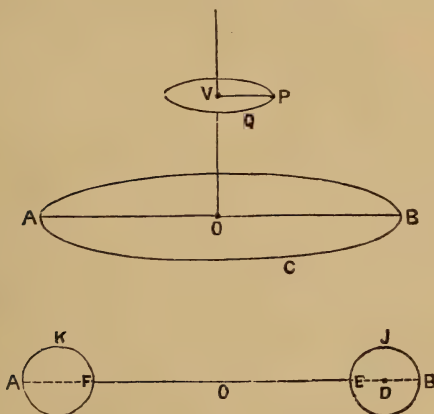
Fig. 2.

Taking a circular strip of radius x and breadth dx at P, the flux of force through the strip is $2\pi Z x\,dx$, i.e.,

$$2\pi \frac{d(Gx)}{dx} . dx.$$

Hence, integrating this from $x=0$ to $x=VP$, we find that the total normal flux through the circle PQ is the value of

$$2\pi Gx \quad \ldots \ldots \quad (3)$$

at P.

Let fig. 2 represent the cross-sections of the wire at A and B in fig. 1 made by a plane through the axis OV, the radius of each being c, while the radius, OD, of the central filament

of the wire is a (as in my paper on the "Magnetic Field close
to the Surface of a Wire conveying an Electrical Current,"
Phil. Mag. August 1893).

Then we shall calculate *the total normal flux of force through
any surface which is intersected once in the positive direction by
every tube of force emanating from the given current.*

This quantity, divided by the current-strength, is the co-
efficient of self-induction of the current.   Taking the general
case, viz., that in which the current-density at every point in
the cross-section of the wire varies inversely as the distance
of this point from the axis OV—we have found (Phil. Mag.
ibid. p. 218) that at any point, P, close to the wire

$$G x = 4ai \left\{ \frac{L}{2} - 1 - \frac{m}{4a} \cos \phi \left[L - 1 - \frac{c^2}{4m^2} \right] \right.$$
$$+ \frac{1}{16a^2} \left[L \left(\frac{3c^2}{4} - \frac{m^2}{2} \right) + \frac{m^2}{2} - \frac{15c^2}{4} \right.$$
$$\left. \left. - \cos 2\phi \left\{ L \frac{m^2}{2} + \frac{c^2}{4} - m^2 - \frac{c^2}{8m^2} \right\} \right] \right\} \cdot (4)$$

where $m = $ PD, $\phi = \angle$ PDA, $L = \log_e \frac{8a}{m}$.

The surface through which we shall take the flux of force
is that which is represented in section by BJEOFKA, *i. e.,* a
surface consisting of the upper half portion of the anchor-
ring formed by the wire and of its central aperture (which
latter is a circle whose diameter is FE).   Obviously this
surface is intersected by all the tubes of force.   Any surface
starting from B and going round to A, *i. e.,* any surface
having the circle of diameter AB for bounding edge, would
do equally well, so far as the above condition is concerned ;
but the calculation is simpler for the first.

The flux through the aperture FE is, then, the value of
$2\pi G . x$ at E, which is obtained by putting $m = c$, $\phi = 0$ in the
above.

Thus the flux through the aperture is

$$8\pi ai \left\{ \frac{L}{2} - 1 - \frac{c}{4a} \left(L - \frac{5}{4} \right) - \frac{c^2}{128a^2} (2L + 19) \right\} . \cdot (5)$$

To calculate the normal flux through the upper half of the
anchor-ring, we must take the value of the magnetic potential,
Ω, at any point close to the ring.   This is the resultant conical
angle subtended by the circuit at the point, multiplied by i ;
and it is therefore (Phil. Mag. ibid. p. 213) given by the
equation

$$\Omega = i \left\{ 2(\pi - \phi) - \frac{\sin \phi}{a} \left(mL + \frac{c^2}{4m} \right) + \frac{1}{16a^2} \left[8c^2(\pi - \phi) \right. \right.$$
$$\left. \left. - \left\{ (6L-5)m^2 + c^2 + \frac{c^4}{2m^2} \right\} \sin 2\phi \right] \right\}. \quad . \text{ (6)}$$

Now the normal force at any point on the anchor-ring is the value of $-\dfrac{d\Omega}{dm}$ with $m = c$; it is therefore

$$i \left\{ \left(L - \frac{5}{4} \right) \frac{\sin \phi}{a} + \frac{c}{16a^2} (12L - 17) \sin 2\phi \right\}. \quad . \text{ (7)}$$

If P is any point on the anchor-ring, the distance of P from OV is $a - c\cos\phi$, and the area of a narrow circular strip of the ring parallel to the plane of the aperture of the ring is $2\pi(a - c\cos\phi) \cdot c\,d\phi$; and this multiplied by (7) is the normal flux of force through the strip. Integrating the product from $\phi = 0$ to $\phi = \pi$, we get the flux through the whole of the upper half of the ring. The result is simply

$$\frac{2\pi ic}{a} \left(L - \frac{5}{4} \right) \int_0^\pi (a - c\cos\phi) \sin \phi\, d\phi,$$

the second term in (7) being neglected because it gives a term of the third order. Thus this part of the flux is

$$4\pi ci \left(L - \frac{5}{4} \right). \quad . \quad . \quad . \quad . \quad . \quad . \text{ (8)}$$

Adding this to (5), we have the whole flux sought, divided by i, equal to

$$\pi \left\{ 4a(L-2) + 2c \left(L - \frac{5}{4} \right) - \frac{c^2}{16a} (2L + 19) \right\}, \quad . \text{ (9)}$$

where $L = \log_e \dfrac{8a}{c}$. This, then, is the Coefficient of Self-Induction. If in this expression a and c are taken in centimetres, the result is the coefficient measured in absolute units; and if this is divided by 10^9, we have the coefficient of self-induction in secohms.

Thus, for example, a circular current running in a wire the diameter of whose cross-section is 2 millim., while the diameter of its central filament is 2 centim., has a coefficient of self-induction of about 59·207 absolute units, or $\dfrac{59 \cdot 207}{10^9}$ secohms; and if the dimensions of the cross-section were neglected, this number would be 58·866.

Clerk Maxwell (Elec. and Mag. vol. ii. art. 704) gives the

coefficient of self-induction as $4\pi a(L-2)$, which agrees with (9) in the principal term.

In the same way we may find the coefficient for a superficial current in the wire. For (Phil. Mag. ibid.) if q is the total quantity of the superficial current, we have the value of Gx at E equal to

$$2q \left[a(L-2) - \frac{c}{4}(2L-1) + \frac{c^2}{16a}\left(L + \frac{11}{4}\right) \right],$$

while from the value of the potential we find the normal flux of force through the upper half of the anchor-ring equal to

$$2\pi qc(2L+1).$$

Hence the Coefficient of Self-Induction is

$$\pi \left\{ 4a(L-2) + 2c\left(L + \frac{3}{2}\right) + \frac{c^2}{16a}(4L+11) \right\}, \quad . \quad (10)$$

which is somewhat greater than the value (9) for a steady current.

XXVI. *Note on the Thermodynamics of the Sun.* By M. P. Rudski, *Odessa*[*].

IT has been advanced by Helmholtz[†] that the contraction of the sun may be the principal source of the energy of that celestial body. He seems to believe that the temperature of a radiating and contracting sun may be rising. On the other hand, Lord Kelvin[‡] esteems such a behaviour highly improbable.

A. Ritter[§] states a theorem, that the temperature of a gaseous celestial body when emitting heat *must* be rising. But this theorem is based on the supposition that the body is in an adiabatic state, contrary to the other supposition that it is losing heat. Mr. Lane[||] has obtained similar results, but the method he has arrived at is unknown to me.

My purpose is to illustrate the assertion of Lord Kelvin, and to define in a certain manner the meaning of the word contraction in the special case which we are considering.

Consider, first, a small body, such as we are observing on

[*] Communicated by the Author.
[†] *Populäre Vorträge*, B. i. pp. 45 & 76.
[‡] Nat. Phil. part ii. (2nd edit.) p. 490.
[§] *Anwendungen der mech. Wärmeth. auf kosmolog. Probleme.* Hanover, 1879, p. 20.
[||] Huggins, Address, Report Brit. Assoc. 1891, p. 18. Mr. Huggins does not quote the book or journal.

the surface of the earth—rigid, fluid, or gaseous. Suppose it uninfluenced by external forces, take the temperature and the volumes as independent parameters but suppose them to be functions of the time. We write the known equation

$$\frac{dQ}{dt} = \frac{\partial Q}{\partial v} \cdot \frac{dv}{dt} + \frac{\partial Q}{\partial T} \cdot \frac{dT}{dt}; \quad \cdot \quad \cdot \quad \cdot \quad \cdot \text{(I.)}$$

where Q, as usual, denotes the heat received from without,

„	v	„	„	volume,
„	T	„	„	temperature of the body,
„	t	„	„	time.

From (I.) we deduce

$$\frac{dT}{dt} = \frac{\dfrac{dQ}{dt} - \dfrac{\partial Q}{\partial v} \cdot \dfrac{dv}{dt}}{\dfrac{\partial Q}{\partial T}}. \quad \cdot \quad \cdot \quad \cdot \quad \cdot \text{(II.)}$$

Daily experience tells us that the right member of (II.) has *always* the sign of $\frac{dQ}{dt}$, i. e. $\frac{dT}{dt}$ has the sign of $\frac{dQ}{dt}$.

There is no doubt that mutual gravitation performs work on the smallest body when it is changing its volume, hence we can admit only two cases :—

(1) The law that $\frac{dT}{dt}$ has the sign of $\frac{dQ}{dt}$ is quite general and applicable to the celestial bodies.

(2) The law that $\frac{dT}{dt}$ has the same sign as $\frac{dQ}{dt}$ holds only for small bodies, because the work of gravitation is so small that the heat generated by these forces may be neglected.

The first case suggests no discussion. For the second take the converted heat into account. Instead of (I.) we have now

$$\frac{dQ}{dt} + \frac{dV}{dt} = \left(\frac{\partial Q}{\partial v} + \frac{\partial V}{\partial v}\right)\frac{dv}{dt} + \left(\frac{\partial Q}{\partial T} + \frac{\partial V}{\partial T}\right)\frac{dT}{dt}. \quad \text{(III.)}$$

V denotes the potential of gravitation. [The mechanical equivalent of heat is supposed equal to unity.] But

$$\frac{\partial V}{\partial T} = 0,$$

since the potential of gravitation does not depend on temperature, and we see that if

$$\frac{dV}{dt} = \frac{\partial V}{\partial v} \cdot \frac{dv}{dt}, \quad \cdot \quad \cdot \quad \cdot \quad \cdot \text{(IV.)}$$

then the equation (III.) is reduced to (I.), and we have again

$$\frac{d\mathrm{T}}{dt} = \frac{\dfrac{d\mathrm{Q}}{dt} - \dfrac{\partial \mathrm{Q}}{\partial v} \cdot \dfrac{dv}{dt}}{\dfrac{\partial \mathrm{Q}}{\partial \mathrm{T}}},$$

and the law that $\dfrac{d\mathrm{T}}{dt}$ has the sign of $\dfrac{d\mathrm{Q}}{dt}$ again holds good.

Consider, now, the meaning of the condition (IV.). Evidently the meaning is that the potential of gravitation should be a continuous explicit function of volume alone. To every infinitesimal variation of volume corresponds an infinitesimal variation of the potential. This condition is realized when the body passes in a continuous manner from one configuration of mechanically stable equilibrium to another. It is evident that, when speaking of the contraction of a celestial body, we mean a " *grosso modo* " continuous passing from one configuration of stable equilibrium to another. Hence, resuming our reasoning, we may say that the temperature of a celestial body, uninfluenced by external forces and radiating heat, must be sinking. But a rain of meteorites (as Lord Kelvin has suggested) may bring quanta of energy sufficient to compensate the loss of heat by radiation, because the sun and a meteorite falling upon it constitute a mechanically unstable system, and the condition (IV.) is not fulfilled.

XXVII. *Changes of Temperature caused by Contact of Liquids with Powdered Silica &c.* By Dr. G. GORE, *F.R.S.*[*]

IT is already known that the physical properties of the surface-layer of molecules of a solid or liquid substance are in some respects different from those of the molecules which constitute the inner portion of the mass, and that those of a very thin film of liquid are not exactly like those of a large bulk. It is further known that solid substances have the power of condensing extremely thin films of liquids, vapours, and atmospheric air upon their surfaces and in their pores, and that the physical properties of the liquids and vapours are thereby modified.

According to Rücker, the specific electric conductivity of a film of soap-solution increases as the thickness decreases (' Nature,' June 1 and October 26, 1893, pp. 116, 625). The superficial film of a liquid is usually very much more viscous than the interior (Daniell, ' Text-book of Physics,' p. 258). According to Overbeck, distilled water offers more, and alcohol less, resistance to the vibrations of a pendulum at its surface than in the interior of its mass (' Nature,' Feb. 24,

* Communicated by the Author.

1881, pp. 397, 398). Pockels states that the surface of water has greater solvent power than the mass, and that a thin disk of camphor partly immersed in a vertical position in water having the cleanest possible surface is cut through in the course of a few hours (*ibid.* March 12, 1891, p. 439). We know that plates of metal partly immersed in a vertical position in corrosive liquids are frequently cut through at the air-contact line : this is often the case with anodes in electrolysis; and I have observed, whilst electrolytically depositing pure grey antimony from its solution, the deposit spread from the cathode over the surface of the liquid as if the surface conducted better than the interior of the liquid. Mensbrugghe, speaking of the cause of surface-tension and evaporation of liquids, concluded that the molecules of the surface-layer of a liquid are farther apart than those of the mass (*ibid.* March 2, 1893, p. 428) ; he also observed that the boiling-point of carbon bisulphide contained in the pores of finely-divided carbon was higher than that of a mass of the free liquid (Phil. Mag. July 1877, p. 43). I have shown that when the molecules of a solid or liquid conducting substance are separated farther apart by solution or dilution, they acquire greater electromotive force due to increased molecular volume (" A Relation of Electromotive Force to Equivalent Volume and Molecular Velocity of Substances," Proc. Birm. Phil. Soc. 1892, vol. viii. pp. 63–138). J. J. Thomson states that, with saline solutions, in some cases the surface-film of the liquid contains more and in other cases less salt per unit of volume than the interior ; and that permanganate of potassium is removed from its aqueous solution by trickling through pure silica ('Applications of Dynamics to Physics,' pp. 191, 192). It has long been known that vinegar is to a certain extent separated from water by pure quartz sand, and that when potato-brandy is filtered through that substance, water passes through first, then alcohol, and finally alcohol plus fusel-oil, as unaltered liquid (Gmelin's 'Handbook of Chemistry,' vol. i. p. 114). Further, in a recent research on the "Decomposition of Liquids by Contact with Powdered Silica," I have found that on agitating various aqueous solutions of acids, alkalies, and salts with finely precipitated pure silica and allowing the powder to subside, the latter substance in many cases abstracts a larger proportion of the dissolved compound than it does of the water, and in a number of cases less (see Proc. Birm. Phil. Soc. 1894, vol. ix. part 1, pp. 1–24), and that in some instances it abstracts more than 80 per cent. of the dissolved substance.

It is generally recognized by physicists and chemists that

the surfaces of mutual contact of two different substances (or of two masses of the same substance in different physical or molecular states) are usually localities of change and transference of energy. Two such substances can rarely be brought into mutual contact without such change occurring, and the changes which occur are more or less different in every different case. In multitudes of cases the changes are of a chemical character, in others they are physical. Volta showed that the mere contact of two different metals rendered them electropolar. Many years ago Pouillet (*Annales de Chemie*, 1822, vol. xx. pp. 141–162), also Regnault (Gmelin's 'Handbook of Chemistry,' vol. i. p. 300), and recently Meissner ('Nature,' Nov. 4, 1886, p. 24), found that when finely divided dry solid substances, such as silica, metals, emery, carbon, &c. were wetted by liquids, such as water, benzol, or alcohol, which have no dissolving or corrosive action upon them, heat is evolved. Pouillet employed many oxidizable substances. Daniell states that when a liquid *begins* to flow through a dry tube, heat is evolved ('Text-book of Physics,' p. 284).

In the present research I have endeavoured to extend our knowledge of the thermal phenomena of this subject. The following is a sectional sketch and a description of the apparatus and method of experimenting.

A is a glass vessel usually containing 50 centim. of the liquid and the bulb of a sensitive thermometer, and is supported in a wire ring having three slender legs. B is a wide glass tube containing 100 grains of finely precipitated pure and dry silica or other fine powder. C is a narrow glass tube open at both ends, and loosely enclosing the stem of the thermometer ; it is supported firmly at its upper end by the clip D, and has fixed securely upon its lower end a conical and very smooth piece of cork which accurately fits the outer tube.

Both the glass vessels A and B are thickly coated with cotton wool.

The thermometer is capable of distinctly indicating a one-hundredth of a Centigrade degree change of temperature, and its bulb is supported a quarter of an inch above the bottom by a small piece of cork.
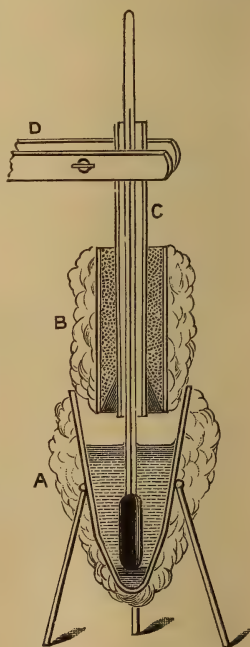
The apparatus is placed in a situation in which the temperature remains sufficiently uniform, and is entirely surrounded by a movable screen of cardboard.

In making an experiment, the powder and liquid were placed near each other in a covered glass vessel in a sheltered situation during a period of sixteen hours, in order to acquire the same temperature. The liquid was then poured into A, and the powder into B, the cup A placed in position beneath with the thermometer immersed in the liquid, and the entire arrangement allowed to stand a sufficient period of time, usually about half an hour, for the solid and liquid to regain the same temperature. The outer tube B was then raised so as to allow the whole of the powder to fall slowly in a thin annular stream into the liquid. The powder entirely surrounded and covered the bulb to a height of one fourth of an inch above its upper end. If the bulb was not sufficiently covered by it, the changes of temperature were less owing to the liquid above being less heated than the powder. The liquid was not stirred in any instance. The act of pouring the liquid into A caused a rise of temperature of about ·03° C., but that of pouring the silica into B had no apparent effect. The maximum rise by contact of the powder and liquid usually occurred in about three minutes. The powders employed were almost wholly different from those used by M. Pouillet, and were such as would not oxidize, and had no recognized chemical action upon the liquid : it is important also to use powders which do not agglomerate or change by use.

Experiments.

Silica with various Liquids.

In all the following experiments with silica, except those otherwise indicated, the weight of silica employed was 100 grains, the volume of solution was 50 centim., and the proportion of dissolved anhydrous substance was 10 per cent. by weight of the water.

The silica was thoroughly purified and ignited previous to each experiment, and was kept in a covered glass vessel during the cooling until it was used. The proportion of cyanogen in the cyanide agreed with that of 100 per cent. KCy; but by evaporating a solution of it to dryness with an excess of sulphuric acid, the weight of sulphate obtained indicated a mixture of 14·45 per cent. NaCy and 85·55 KCy.

The following Table shows the results of the experiments with silica.

TABLE I.

Experiment.		Cent. Degree.	Experiment.		Cent. Degree.
1.	Na_2CO_3	·04	30.	AmCl	·30
2.	$NiSO_4$	·10	31.	Na_2HPO_4 (5·0 per cent.)	·30
3.	$NaHCO_3$	·12	32.	$KHSO_4$	·30
4.	$SrCl_2$	·12	33.	$SrCl_2$ (20·0 per cent.) ...	·30
5.	$BaCl_2$	·13	34.	H_2O....................	·30
6.	$MnSO_4$	·14	35.	NaCl	·32
7.	Na_2SO_4	·15	36.	$FeCl_2$	·33
8.	$MgSO_4$	·15	37.	HNO_3	·34
9.	$KClO_3$ (5·0 per cent.)	·15	38.	K_2CO_3.........................	·36
10.	$CaCl_2$	·18	39.	KBr.........................	·37
11.	$AmNO_3$	·18	40.	Acetic Acid................	·37
12.	Tartaric Acid	·18	41.	$FeSO_4$.........................	·38
13.	HIO_3	·19	42.	KBr (Note "A")	·38
14.	$ZnCl_2$	·20	43.	$MnCl_2$.........................	·39
15.	CrO_3	·21	44.	$ZnSO_4$.........	·41
16.	K_2SO_4	·22	45.	$MgCl_2$	·41
17.	$CoSO_4$.....................	·23	46.	$CdCl_2$	·41
18.	AmBr	·24	47.	H_2SO_4.........................	·42
19.	NaBr	·24	48.	H_3PO_4.........................	·44
20.	Am_2SO_4	·24	49.	$KHCO_3$	·44
21.	$CuSO_4$.....................	·25	50.	$H_4P_2O_7$	·47
22.	Citric Acid	·25	51.	HCl.........................	·48
23.	KI	·26	52.	KCy (1·25 per cent.)......	·60
24.	KNO_3	·26	53.	KCy (2·5 „ „)......	·67
25.	HBr.........................	·26	54.	KCy (5·0 „ „)......	·70
26.	LiCl.........................	·28	55.	NaCy	·72
27.	$SrCl_2$ (5·0 per cent.) ...	·28	56.	$CdSO_4$.........................	·78
28.	$CoCl_2$	·29	57.	KCy.........................	·82
29.	KIO_3 (5·0 per cent.) ...	·29	58.	AmHO ....1·40

Note "A," exp. 42.—In this case the silica was exposed in an uncovered vessel to the air during sixteen hours, but this had only a minute influence upon the amount of rise of temperature (compare with No. 39).

Remarks.—In every one of the instances of Table I. a rise of temperature occurred; as, however, water alone gave a rise and was used as the solvent in all cases, this circumstance may explain that uniformity of result. Whilst many of the solutions gave larger rises than water, quite as many gave smaller ones; and we may regard all those which gave smaller ones as containing substances which *absorbed* heat and diminished the rise, whilst those which gave larger ones *evolved* heat and added to the amount of rise produced by water alone. Probably by further research some substances may be found which will more than neutralize the temperature-effect of the water and give negative numbers.

The series of results obtained with potassium cyanide in exps. 52, 53, 54, and 57 show that the magnitude of rise of

temperature increased with the strength of the solution ; but those produced by strontium chloride in exps. 4, 27, and 33 do not appear to afford consistent results : whether this was due to differences of molecular constitution of the dissolved substance I have not investigated.

Influence of Size of the particles of Silica.

Exp. 59.—With 50 centim. of the 10-per-cent. solution of potassium cyanide and 100 grains of coarse quartz sand, the particles of which averaged about one sixteenth of an inch in diameter, the rise of temperature was only ·03 C. degree, whilst that produced by the same weight of the precipitated silica was ·82 C. degree (see exp. 57), or 27·3 times as much. These results indicate a method of ascertaining the average magnitude of the particles of insoluble powders.

Alumina with various Liquids.

In each of the following cases, 200 grains of alumina and 50 centim. of 10-per-cent. solutions of the substances were employed. The alumina was precipitated from a solution of alum by means of ammonia, then thoroughly washed, and finally heated to redness, and was very pure.

TABLE II.

Exp.		Cent. Degrees.	Exp.		Cent. Degrees.
60.	$KHCO_3$	·50	71.	NaBr	1·70
61.	Am_2SO_4	·54	72.	AmCl	1·76
62.	$SrCl_2$	·59	73.	$CdSO_4$	1·86
63.	Na_2CO_3	·74	74.	$CdCl_2$	1·38
64.	KCy	1·07	75.	Na_2SO_4	2·06
65.	H_2O	1·16	76.	AmSesquicarb.	2·25
66.	KCl	1·34	77.	$MgSO_4$	2·34
67.	$ZnSO_4$	1·55	78.	K_2CO_3	2·40
68.	$MgCl_2$	1·64	79.	$CuSO_4$	2·40
69.	AmHO	1·64	80.	KBr	2·45
70.	KNO_3	1·66	81.	NaCl	2·58

In every instance with alumina a rise of temperature occurred : the probable explanation of this, however, is similar to that with silica.

Remarks.—Although a 10-per-cent. solution of common salt produced so large a rise of temperature by contact with alumina, it only lost 1·1 per cent. of dissolved substance (see

"Decomposition of Liquids by Contact with Powdered Silica," Proc. Birm. Phil. Soc. 1894, vol. ix. pp. 1–24) ; and it was not rendered alkaline to test-paper.

Various Powders with Water and Ammonia.

TABLE III.—With Water.

Exp.		Grains.	C. Deg.	Exp.		Grains.	C. Deg.
82.	$BaSO_4$	300	·00	88.	$MgCO_3$	100	·11
83.	$SrCO_3$	200	·05	89.	Fe_2O_3	150	·12
84.	$CaCO_3$	100	·05	90.	SnO_2	200	·18
85.	PbO	400	·08	91.	MnO_2	300	·47
86.	Cr_2O_3.........	50	·10	92.	Al_2O_3.........	200	1·16
87.	$BaCO_3$	200	·10				

TABLE IV.—With 10 per cent. Aqueous Ammonia.

Exp.		Grains.	C. Deg.	Exp.		Grains.	C. Deg.
93.	$CaCO_3$	100	·06	99.	SnO_2	200	·22
94.	$SrCO_3$	200	·08	100.	Cr_2O_3.........	50	·52
95.	$BaCO_3$	200	·10	101.	PbO	400	·53
96.	$BaSO_4$	300	·15	102.	MnO_2	300	·90
97.	$MgCO_3$	100	·17	103.	MnO_3.........	200	1·64
98.	Fe_2O_3	150	·18				

The volume of liquid in each case was 50 centim. Washing the barium sulphate with a 10-per-cent. solution of ammonia, then with water, and finally heating to redness, hardened it. In the above experiment (No. 96) it was not washed with ammonia.

General Remarks and Conclusions.

It is evident, that as in all cases the formation of a liquid film upon the surfaces of the solid particles must have been attended by the destruction of an air-film, and the latter action was probably accompanied by absorption of heat (different in amount with different powders), the observed rise of temperature did not represent the whole of the heat evolved by contact of the liquid and solid. Consequently it is possible that in those cases in which little or no rise of temperature was observed, the amount of heat absorbed by the liberated air may have been equal to that evolved by the uniting liquid.

In all the experiments the formation of a liquid film evolved a larger amount of heat than that absorbed by the air-film which it displaced.

The further fact must not be overlooked, that in all these experiments there existed a minute source of error which could not be avoided, viz., that although each powder employed appeared to be perfectly wetted in ten or twenty seconds, it was not so, but continued to evolve a very small quantity of minute bubbles of air after that period. With peroxide of iron this action ceased in about half an hour, and with silica and alumina it continued during several days; but even in the latter cases it was probably not sufficient to affect the general result to an extent of a one-hundredth part.

As all the observations of maximum rise of temperature were compelled to be taken at the moment they occurred, viz., in about three minutes after mixing, any amount of heat evolved after that period could not be included. Even when a separate portion of the powder was thoroughly shaken with some of the liquid in a bottle, the bubbles similarly appeared, but with coarse white sand they did not occur. Another circumstance (which has already been mentioned) is that the temperature of the immersed powder was higher than that of the liquid above it.

The general results confirm the conclusion arrived at by previous investigators (Pouillet and Meissner), that in all known cases the contact of a liquid with an insoluble powder evolves heat. From the present ones, however, in which organic and oxidizable substances were avoided and only water and aqueous solutions were employed, it appears probable that (subject to the foregoing considerations), whilst many dissolved substances evolve heat and add to that produced by the water, a large number absorb heat and subtract from that effect: with silica nearly half the number of solutions evolved less than water alone.

In all aqueous solutions the change of temperature appears to be attributable to several causes, viz.:—1st, the union of the water with the powder; 2nd, that of the dissolved substance with the powder; and 3rd, the separation of the film of air; and the rise of temperature is reasonably explained by the general view that a degree of mechanical union takes place of the powder with the water or with the dissolved substance, the powder abstracting from the liquid, either some of the water or of the dissolved substance or of both (see "Decomposition of Liquids by Contact with Powdered Silica," Proc. Birm. Phil. Soc. 1894, vol. ix. pp. 1–24).

If we compare the order of magnitude of rise of tempera-

ture with that of amount of dissolved substance abstracted by the powder (*ibid.*), we find that the two do not usually vary together. This is a result which might be expected if the amount of change of temperature depends upon all the conditions above suggested, and especially as it further depends in many cases upon heat absorbed by contact of the powder with the dissolved substance.

The fact that the portion of dissolved substance which unites with the powder is entirely removable by washing with water proves the reversibility of the action, and that the phenomena are essentially the same as those of chemical union and separation in reversible cases (*ibid.*). The substitution also of a film of water or solution for one of air in contact with the powder must obey the same general laws as that of substitution in recognized chemical actions. And we may further reasonably infer that whilst the union of the water or of the dissolved substance with the powder is usually attended by evolution of heat, the separation of the film of air from the powder is frequently accompanied by absorption of heat.

As the action is purely a surface one, and the amount of rise of temperature increases with that of immersed solid surface, it is essentially the same whether the amount of surface is obtained by means of large particles or small ones.

As the union of the water or the dissolved substance with the powder is attended by loss of molecular energy, the action must be due to both of the touching substances, and must obey the law of equality of action and reaction, a portion of the molecular motion of each substance being neutralized and changed into heat, and the molecules of the liquid which have lost motion must remain nearer to the solid, or, in ordinary terms, "adhering" to it. The amount of heat set free by the "adhesion" of the liquid to the solid is probably dependent both upon the mass and the loss of velocity of the "adhering" molecules. As nearly the whole of the change of temperature caused by the "adhesion" occurred in a few minutes, the mutual loss of molecular energy by the two substances must have quickly ceased. After the evolution of heat has ceased there remain permanent changes of superficial molecular state and a new condition of balance between the different sets of molecules present, until by washing and subsequent heating the powder is restored to its original state.

The reversibility of the action, and the new state of molecular balance intervening between the evolution of heat by wetting the powder and the absorption of heat by drying it, is analogous to cases of reversible chemical union, to the sudden electric charge of two different metals by mere con-

tact, the ensuing state of steady charge and the subsequent discharge ; and may be further compared with the effects of approach and withdrawal of magnets and their armatures, and with the commencement and cessation of electric currents by magnetoelectric and dynamoelectric induction. All these five actions are reversible ones, attended by molecular change, disturbance of the æther, and transference of radiant energy at the moments of commencement and termination, with a new state of molecular balance but no external dynamical effect during the intervening statical period, and by an undoing of the first dynamical effect by the second one in each class of cases. They are all evidently based upon similar mechanical principles of molecular motion.

As the quantity of heat evolved per given weight of potassium cyanide in experiments 52, 53, 54, 57 was larger the more dilute the solution, the amount of loss of velocity, and the actual velocity of the molecules of that salt were greater the more dilute the solution. The latter conclusion agrees with the observation that the voltaic electromotive force of a dissolved substance is usually increased by dilution (see " A General Relation of Electromotive Force to Equivalent Volume and Molecular Velocity of Substances," Proc. Birm. Phil. Soc. 1892, vol. viii. pp. 63–138).

In proportion as the amount of heat evolved is greater, the degree of " adhesion " is stronger and partakes more of the character of ordinary chemical union. Each particle of the powder " adheres " both to the solvent and to the dissolved substance probably in all cases, but in each case apparently in different proportions (*ibid.* 1894, vol. ix. pp. 1–24). If the powder " adheres " to a larger proportion of the dissolved substance than it does to that of the solvent, the " adhering " film of liquid is a more concentrated solution than the remainder, but if it " adheres " to a smaller one the opposite effect occurs ; but in either case chemical analysis of the separate portion of liquid reveals the change and affords data for comparison with the alterations of temperature, total amount of heat, &c.

The easily formed anticipation that the amount of rise of temperature produced by a given weight of silica increased with the degree of smallness of the particles was verified by actual experiment. Thus the rise produced by 100 grains weight, consisting of 1037 particles of coarse sand, by immersion in 50 centim. of a 10-per-cent. solution of potassium cyanide, was only ·03 C. degree, whilst that produced by the same weight of the finest precipitated silica, after washing and heating to redness, was ·82 C. degree (*see* Experiments

57 and 59), or 27·3 times as much. If the proportion of in-
crease of temperature to that of surface were known, the
average magnitude of the particles of the finest insoluble
powder might perhaps be calculated.

The evolution of heat by the mere contact of solids and
liquids which do not in the ordinary meaning of the term
" chemically unite," must to a minute extent affect the de-
termination of the specific heats of insoluble powders by the
method of mixing them with water. And if contraction of
volume follows immediately upon its loss of heat, then the
specific gravities of insoluble powders when arrived at by the
process of weighing them, first in air and then in water, are
probably also slightly influenced.

The heat produced by the mere contact of insoluble solids
such as silica, alumina, &c. with water and aqueous solutions
of salts, may account for that produced by spring-water, sea-
water, mineral-water, &c., filtering through geological strata,
and for that developed in other cases of underground tem-
perature where ordinary chemical action is absent.

XXVIII. *On the Limits of Vision: with special Reference to
the Vision of Insects. By* G. JOHNSTONE STONEY, *M.A.,
D.Sc., F.R.S., Vice-President, Royal Dublin Society* [*].

CONTENTS.

Introductory Remarks.

THE President of the British Association, at the recent
meeting of that body in Nottingham, mentioned in his
opening address that the image formed by the compound eye
of an insect had been photographed. This suggests the
inquiry how the image is formed, and what is the limit of the
vision of which it is the physical basis. The investigation of
this point shows that insects cannot see very minute objects,
and the whole inquiry seemed of sufficient interest to be laid
before the Royal Dublin Society, especially as it suggests
much further study which the author could not attempt, but
which there are other members of the Society most competent
to undertake.

SECTION I.—*Of Vision in general.*

As preliminary to the inquiry it is well to consider what are the causes that limit the amount of detail that can be seen by the instrumentality of eyes such as our own, the kind of eyes of which we know most. That there is such a limit to human vision may be easily seen by placing a well-illuminated ruling of parallel lines at different distances from the eye of a person whose vision is good. Let us suppose black lines ruled, as in fig. 1, on a white surface at intervals of one millimetre from the middle of one line to the middle of the next. If an observer with keen vision views these from a distance of eleven or twelve feet, he is able barely to make out that they are a ruling ; beyond that distance, they seem one uniform grey surface, while from stations nearer to them he perceives the individual lines distinctly.

Fig. 1.

Millimetric Ruling.

Now, at a distance of eleven feet a millimetre subtends an angle of 1′ (one minute). Hence we learn from observation that in order that two objects may be seen as two, they must, at least, subtend an angle of about 1′ at the eye. If they subtend a less angle than this they are seen as one object.

Now there are three distinct causes, any one of which is by itself competent to put a limit of this kind to our power of distinguishing minute objects ; and in persons with the best vision each of these three seems to put nearly the same limit as the other two. This adjustment between them is, no doubt, the result of development, since any further improvement on the lines of any one of these causes would be useless, unless it were accompanied by a simultaneous improvement in both the others.

One cause is the spacing of the cones that occupy the *fovea lutea*, into the small area of which about 7000 are packed. The *fovea lutea* is that spot in the retina which furnishes us with the exceptionally distinct vision which we have in the middle of the field of view. The cones are here without accompanying rods, and are at intervals of about 4μ *, measuring from the middle of one to the middle of the next. This interval is about half the diameter of the red corpuscles

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* The micron μ is the millionth part of a metre. This is the same as the thousandth of a millimetre, or the 1/25400th of an inch.

of human blood, an object familiar to every microscope-observer. Again, the "optical centre" * of the eye lies a centimetre and a half in front of this part of the retina ; and at this distance the interval between adjoining cones subtends an angle of nearly 1′. Hence, in order that the images of two points of light may fall on the corresponding parts of different cones, their distance asunder must subtend an angle of, or exceeding, 1′ at the optical centre of the eyes ; in other words, the interval between the objects in external nature that are being examined must subtend this angle at the eye. Thus we fail to see with the unassisted eye much detail which is revealed to us by the microscope. This happens if at a distance of ten inches, the distance of most distinct vision, the intervals at which these objects are spaced subtend an angle of less than 1′. Such objects may, however, be seen with optical aid, provided it is such that the little interval subtends an angle exceeding 1′ at the optical centre † of the object-lens used in the microscope, a point which, with the higher powers of the instrument, lies close to the object on the stage. But beyond this limit, and therefore beyond the reach of the microscope, there are still worlds of events in nature which we can never see, although we may infer the existence of some of them in other ways.

We have found that the spacing of the cones in the *fovea lutea* is competent to put a limit to the minuteness of the detail that can be seen with the naked eye. Now, the small size of the pupil of the eye also, and independently, determines such a limit. Astronomers are familiar with the fact that the image of a star (which is virtually the image of a point of light, since no telescope is competent to show the true disk

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* From each point of a visible object a cone of rays, starting from that point as its apex, falls on the pupil. In passing through the eye this cone of rays is made to converge, and finally becomes a cone of rays advancing towards that point of the retina where the image is formed. The apex of the second cone is accordingly at this point. Most of the rays of the first cone are bent in passing through the cornea and optic lens, and advance in a new direction in the second cone. But there is one among them, which, in the second cone, continues in the same direction, or at least parallel to the direction which it had in the first cone. This ray is called the undeviated ray. It is easily seen that there is one such ray in the light coming from each point of the object. Now all the undeviated rays very nearly pass through a certain point which is situated close behind the optic lens, and $1\frac{1}{2}$ centimetre in front of the middle of the retina. This is the point which is called the "optical centre" of the eye.

† The optical centre of the object-lens of a microscope is the point where the "undeviated rays" cross (see last footnote). In compound microscopes this point lies in or in front of the object-lens, and with high powers is close to the object.

of a star) consists of a small round central patch called the spurious disk, surrounded by coloured rings which very rapidly fall off in brightness. This phenomenon is due to the interference of the light coming from the two halves of the object-lens, and is susceptible of mathematical treatment. It thus appears that the angular radius of the first dark ring, estimated from the middle of the object-lens, is

$$\theta = (1 \cdot 22) \frac{\lambda}{A},$$

where λ is the wave-length of the light, and A the aperture, *i. e.* diameter, of the object-lens. This furnishes a boundary within which the central spurious disk lies, and up to which its faintest outlying portion barely extends. It also fixes the *minimum visibile* with that aperture, since two points would have begun to be blurred into one another if so close that the middle of the spurious disk of each lay on the first dark ring of the other. Let us then put into this formula, $\theta = 1' = \cdot 00029$ in circular measure (this is the limit already fixed by the rods and cones), and $\lambda = \cdot 6$ of a micron (which is the wave-length of yellow light). We thus find

$$\cdot 00029 = (1 \cdot 22) \frac{\cdot 6}{A}$$

whence $A = 2524$ microns, which is very nearly $\frac{1}{10}$ of an inch. This, then, is the diameter of the pupil of the eye when of such size as to put the same limit on the visibility of small objects as the rods and cones do. Now, this is about the size to which the pupil of the eye shrinks when we scrutinize well-illuminated objects, and is the smallest to which it can be allowed to shrink without interfering with the vision of minute detail, by placing a further restriction beyond that imposed by the layer of rods and cones [*].

Again, the eye viewed as an optical instrument is far from perfect. Its chromatic defect may be detected by placing the finger horizontally in front of the eye, and looking just over it at the bar of a window. In this way the window-bar is viewed through the upper half of the pupil, and is then seen

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[*] It might be thought that with the more dilated pupil which we have in faint light, we could see more detail. But the reverse is the case; for instance, the two small double stars ϵ_1 and ϵ_2 Lyræ are more than 3' asunder, and yet, in consequence of their faintness, are nearly at the limit of what a very good eye can see distinctly as two objects. To eyes that are fairly good they appear as one object elongated, while persons may have tolerably good sight and not even see the elongation.

to be bordered with colour. Finally, the spherical aberration*
of the eyes becomes conspicuous when we view a considerable
star or planet with one eye. Instead of being seen as a point,
it is seen as a small irregular patch with short tails from it,
and of somewhat different shape according as it is viewed with
the right or with the left eye. Now this is due to spherical aber-
ration co-operating with another defect which it is difficult to
disentangle from spherical aberration, and which is caused by
the light having to pass through the other layers of the retina
before reaching the rods and cones. These layers, however,
do little harm in the *fovea lutea*, as here they are either
absent or thin, so that the irregular image seen when we look
directly at a planet is chiefly due to pure spherical aberration.

Now these defects, viz. the chromatic and spherical aberra-
tions, including under the latter that further defect which
arises while the light is crossing the retina, are dealt with in
nature in the same way in which a photographer deals with
them in his photographic camera, viz. by limiting the aperture,
which diminishes the effect of these imperfections. We have
already found that the aperture of the pupil is contracted
as much as is compatible with the other conditions to be
fulfilled. Now it is evident that a certain amount of the
defects with which we are at present dealing, especially when
rendered less operative by the limited aperture of the pupil,
may be allowed to remain in the eye without rendering it
incapable of distinguishing objects separated by 1′ of angle,
the limit already fixed by the rods and cones; and there can
evidently be no tendency in evolution to effect any further
improvement of the eye as an optical instrument. Accord-
ingly, in persons with the best vision, the eye seems to have
been just improved up to this point, leaving its outstanding
defects still very conspicuous when searched for; and it is
shortcoming in respect to these defects which is chiefly what
makes one man's eyesight less perfect than another's.

We shall next deal with another preliminary remark,
which it is well to make, as it will dispel the oft-repeated
error that there ought to be some connexion between our
vision and the position of the image formed on the retina.
It is pertinent to point this out when engaged in inquiring
into the vision of insects, for, as we shall see presently, the

* If a sphere be drawn round a point of the image formed by light of
one wave-length, to represent the crest of one of the luminous waves
advancing towards that point, the whole of the crest should reach that
sphere at the same instant of time. There are, however, usually little
deviations of some parts of the crest of the wave from this sphere, which
defect is called spherical aberration.

image formed by compound eyes is erect, while that formed by single eyes, such as ours, is inverted. Neither position, however, nor a sideward position, nor any other, would be incompatible with our seeing the objects of the world around us exactly as we now do. For the direct physical adjunct of a visual perception in our mind of a point of the object, is not any event in the eye or along the optic nerve but in a more deep-seated part of the brain, probably in its occipital lobes which lie in the back of the head, over the cerebellum. Now (speaking from the physical stand-point) the way in which this event in the occipital lobe is usually evoked is by light from the point of the object being guided through the eye to one of the rods or cones, after which some event travels along one of those nervelets with attendant nerve-cells which penetrate the retinal layer from the expansion of the optic nerve, and each of which is asso-ciated with one individual rod or cone. This is succeeded by some event along one fibril of the optic nerve, after, which there seem to follow other events within the brain, which finally lead up to *that particular event* which, and which alone, is the true physical adjunct of the visual perception in our mind—our perception of that point of the object from which the light set out to enter the eye. I, for convenience, speak of this event as situated in the occipital lobe, although its location can hardly be said to be ascertained.

Now it is evident that the image on the retina is only one link in this long chain of physical causes and effects, and that the image might be erect as it is in the compound eyes of insects, or inverted as in our eyes, or might have any other orientation, and that nevertheless the positions of the rod or cone, nervelet, fibril of optic nerve, &c., could be so disposed as to produce precisely the same final event within the occipital lobe of the brain, as now occurs. Now it is this last alone which is essential, the others being only instrumental in bringing it about: it alone is the true physical adjunct of the visual perception which becomes part of the mind.

Again, although the train of causes and effects described above is the usual process by which this adjunct of percep-tion is evoked, it is not by any means the only way in which it can be brought about, as is conspicuously manifested by dreams, and may be detected by a careful introspective study of the memory of visual perceptions. I am of opinion that in all cases, when remembering a past scene, there is some dim, usually a very dim, recurrence of the perception, or of parts of it : at all events, under some circumstances, this is dis-tinctly the case. When, unfortunately, we lie awake for

several hours, especially under the influence of tea or coffee, until a feeling of weariness and an indisposition to any prolonged train of consecutive thought have come over us, I have observed that the revival of visual perceptions, when thinking about past scenes, becomes stronger and is easily perceived, and that in some cases it may become almost vivid. In extreme cases it even amounts to a kind of dreaming with the eyes open—the dream, however, differing from ordinary dreams by being one the progress of which we can ourselves direct. It is important to note that these visions are not based on any affection of the retina, and in this respect differ wholly from those spectral images which we see after gazing for some time at objects which somewhat dazzle the sight. These latter shift their position with every movement of our eyeballs ; the others retain what we estimate to be their positions in space, notwithstanding that the eyes be moved about. Now this is very significant. It shows that the train of physical causes which lead up to that event in the posterior lobe, which is the adjunct of our perception of these visions, did not originate in the retina, but in a part of the brain where it could arise in conjunction with some of those events which are the physical adjuncts of our judgments about space. This is an important conclusion to have reached.

What is probably in reality only a further stage of these waking dreams is sometimes experienced in fever, when the patient has been for days without sleep. I myself saw apparitions in this way, after having been three days without sleep, those I saw having a marvellous appearance of reality, and being seen in the daylight when I could at the same time see in the ordinary way the objects about me in the room, except where one of these novel figures intruded. In these places the connexion with the retina seems to have been rendered more or less inoperative, and a visual perception, otherwise produced, was substituted for the ordinary one.

Another instructive and more agreeable way of making the observation is to experiment on ourselves when in that stage of drowsiness in which we seem to have fallen partially asleep, but not so much so but that we can still voluntarily direct our thoughts to some well-remembered scene, or, still better, first to one, and afterwards to another. If we repeatedly seize opportunities of making this experiment, we shall gradually accumulate instances of every degree of vividness, from the full distinctness of a dream in respect of colour, brightness, and form, down to the shadowy dimness of what we very imperfectly see in the exercise of ordinary memory. The same important observation may be made here as on a

former occasion. The objects so seen do not shift their positions when we voluntarily move our eyes about. They have their origin not in the retina, but in immediate connexion with the part of our brain which is directly related to our judgments about space.

Another interesting observation is of what happens when we get into what is sometimes called a " brown study "— thinking intently upon some past scene that engrosses our attention. On such occasions the visual image before " our mind's eye " becomes more vivid than usual, and in the same degree the image produced in the ordinary way of the external objects towards which our eyes may chance at the time to be directed becomes less distinct, and, in extreme cases, may almost fade out, so that even noteworthy events may happen in our presence which we do not see, or at least which do not impress us sufficiently for us to retain any memory of them.

Two experiences, one of a friend and one of myself, seem worth recording in this connexion :—

Some years ago this friend and I rode —he on a bicycle, I on a tricycle—on an unusually dark night in summer from Glendalough to Rathdrum. It was drizzling rain, we had no lamps, and the road was overshadowed by trees on both sides, between which we could just see the sky-line. I was riding slowly and carefully some ten or twenty yards in advance, guiding myself by the sky-line, when my machine chanced to pass over a piece of tin or something else in the road that made a great crash. Presently my companion came up, calling to me in great concern. He had seen through the gloom my machine upset and me flung from it. The crash had excited the thought of the most likely cause for it, and the event in his brain, which was the physical adjunct of the thoughts thus passing through his mind, were so associated with that other event in the brain, which is the adjunct of visual consciousness, that the one (speaking from the physical stand-point) evoked the other, perhaps faintly. This involved a visual perception in the mind faint, but sufficient on this occasion to be seen with sufficient distinctness when not over-powered by objects seen in the ordinary way through the eyes.

The experience I had myself was one which frequently occurred to me when a lad. Several of us boys were fond of witnessing sham fights in the Phœnix Park, at which some of the most conspicuous objects were the single horsemen who now and then galloped at full speed, with orders, from one part of the field to another. Almost always, after a day spent in viewing this spectacle, as I lay in bed at night I saw

vividly what seemed to be a tiny horseman galloping violently from right to left, or from left to right, as the case might be. All the movements of the horse were reproduced, the dashing about of the sabre-tasche, the coloured uniform, the movements of the horseman. It cannot have been in the retina that this revival took place. It must have been in a much more deep-seated part of the brain.

It would, I think, be of very great interest to ascertain from the inhabitants of a blind asylum, whether those who have recently had their retinas extirpated, or rendered functionless, continue to dream of scenery, so long as the memory of visual perceptions is recent. I should expect they would, as the structures which they have lost do not seem to be concerned in either memory or dreaming.

From a review of all the evidence it appears clear that the retinal image is only one of the stepping-stones in a rather long progress from the object in nature to the event in the brain which is the direct adjunct of visual perception. Why, then, it may be asked, is an image necessary? Why is it never absent? Why is not something quite different sometimes substituted for it? The following is, I think, a sufficient answer. There must be *some difference* in the events occurring in the occipital lobe in order that two points of an object may be seen distinct from one another. To bring this about either a different nervelet must have been acted upon in the organ of sight, or the same nervelet must have been differently acted on. In the case that actually occurs, it would appear that a different nervelet is acted upon when the points of the object are sufficiently separated to be seen as two, and that a difference of action on the same nervelet is reserved for exhibiting to us variations of brightness and colour, but not of position. Now this can manifestly be effected by distributing the points of an image of the object over an apparatus such as the layer of rods and cones, consisting of closely packed individuals, each of which is capable of acting on its own nervelet; or through an intermediate apparatus, which consists of channels for transmitting light as numerous as the rods and cones, each of which conducts the light from a specific point of the image to its own rod or cone, which latter may, in this case, be situated at a distance from the place where the image is formed. The first of these is the arrangement which we find in our own eyes; the other seems to be that which we find in the compound eyes of insects. Now it is doubtful whether any other machinery for bringing about the result than one or other of these two can be devised. These, at all events, are the ways in which nature attains the end; so that neither man nor nature seems to have found out

any other. But the position of the images, whether erect, inverted, or any other, is obviously immaterial. It is the ultimate effect within the occipital lobe of the brain that is alone essential.

Section II.—*Of Vision with Compound Eyes.*

After these preliminary remarks on vision in general, we seem to be in a position to deal intelligently with the inquiry—How is the retinal image formed in insects? and what kind of vision do they enjoy through the instrumentality of the compound eyes with which they are furnished? These questions may be most conveniently dealt with by describing a rough model of an insect's eye. Imagine a hemispherical shell of some transparent material, *e. g.*, half of a sixteen-inch globe of glass, that is, a globe of which the diameter is sixteen inches. Place your eye at its centre, and look through it at the objects of nature around you. Next, let an accurate picture of these objects be painted on the outside of the globe, so that when you place your eye at the centre you still see the same scene as before. Now let a network of scratches be made all over the painting, dividing it into patches, each of which is the size of a square quarter of an inch. This is about the size of the cross section of a lead-pencil. There will be about 6400 of these patches on the hemisphere. Next, let the paint of each patch be removed, and a single dab of paint substituted, of a tint and brightness which is the resultant of the part of the picture which fell within the patch. In this way, a somewhat coarse mosaic is substituted for the more perfect picture of the external world previously drawn. This coarse mosaic gives a rough imperfect representation of the external world, and represents correctly the vision which an insect has of it. The compound eyes of some insects, especially insects that attack other insects, have more numerous facets than what correspond to 6400 over a hemisphere; and in such cases the mosaic is less coarse, and the vision is proportionately better. Thus the eye of a dragonfly is better represented by substituting smaller patches, each the size of a square eighth of an inch. This increases the number over the hemisphere to 25,600. But there is a somewhat narrow limit to improvement in this direction, owing to its necessitating a diminution of the aperture of the lenses. The way that nature deals with this difficulty is by increasing inordinately the size of the compound eye of the insect out of proportion to its other features. In this way the number of the patches, one of which is formed by each facet, can be

increased without diminishing too much the aperture of the little lenses.

With a mosaic such as is described above, the diameter of each patch subtends about a degree and eight-tenths (1°·8) at the centre of the hemisphere. Accordingly, the interval between two objects in nature would need to subtend an angle of about a degree and three-quarters at the insect's eye, to be distinguishable as two by the insect. Hence, if as far off as ten inches, the distance at which we see most distinctly, they would need to be separated by nearly the third of an inch to be seen by the insect as more than one object ; while, if close to the insect, only one-tenth of an inch off, the separation would need to be about the same as that which the human eye is capable of distinguishing at a distance of ten inches. Thus, the insect cannot see more detail upon its own antennæ, close as they are to it, than we can with our naked eye. We must, therefore, dismiss from our thoughts the mistaken impression that insects see very minute objects far beyond human vision. On the contrary, their vision is imperfect compared with ours. Still, it is evidently quite enough to enable a bee to be guided in its search after honey by the markings upon a flower, or effectually to assist a fly in its wanderings about the room, or in sopping up its food.

We have next to consider how this mosaic is formed. For this purpose let us again turn to our model. Suppose 6400 hollow conical funnels to be provided, each one inch long. Let them be slightly more than the thickness of a lead-pencil at their larger end, and tapering from this down to a diameter of a sixteenth of an inch at their smaller end. Let the insides of these funnels be blackened so as to stifle any light that falls on them. Fit a small lens of one-inch focus into the larger end of each, and then pack the funnels somewhat like the cells of a honeycomb, over the hemisphere spoken of above, the larger

Fig. 2.—The Funnels of an Insect's Eye (diagrammatic).
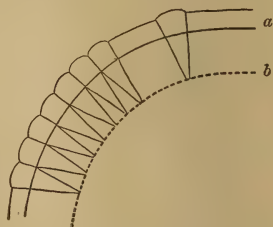
a. Outer surface. *b.* Primary surface.

ends outwards, and the smaller planted on the middles of the little patches that were marked out on the hemisphere. The little lenses will then lie on an outer hemispherical sheet eighteen inches in diameter.

Let us fix our attention upon one of the little lenses, and consider how it operates. The light from distant objects in-

the external world would, if not interfered with, form an inverted image one inch behind this lens, that is, at the distance of the glass hemisphere, which we shall call the primary surface ; but it is prevented from forming more than one patch of that image by the blackened walls of the funnel. Accordingly, only one tiny patch of the image, one-sixteenth of an inch across, is actually formed. It is formed by the light which passes the whole way down the funnel and, emerging at its end, falls on the surface of the primary hemisphere. Here it produces one little fragment of the inverted image, the rest of the image which the lens is competent to form being extinguished by the blackened walls of the funnel. In the insect's eye the small portion of the image that emerges is, no doubt, a portion of a rather indistinct image, owing to the very small aperture of the lens ; but neither this nor its belonging to an inverted image is any detriment, since all the rays that go to form the little patch are transmitted to a single one of the pieces of apparatus in the insect, corresponding to the rods and cones in our eyes. They, therefore, can result in only one of the optic nervelets being affected, and in some one definite way ; in other words, the whole of the light forming one patch, or rather speck, of the image can produce only one elementary visual impression in the insect's mind.

It will be observed that the image that is formed resembles rather a mezzotinto engraving, which consists of separate specks, than a mosaic which consists of patches of colour large enough to touch one another ; and that it differs from the mezzotinto in that the specks are specks of light, instead of being, as in the engraving, specks of shade.

If we endeavour to make out what provision is made in compound eyes for enabling the insect to accommodate its vision to varying distances of the object, we find, upon a scrutiny of the section of such an eye, that the arrangement appears to be one which gives to an insect the very singular power of adjusting different parts of its field of view to different distances, and operates in a remarkably simple way which may be illustrated upon our model if we add somewhat to it. For this purpose let a third hemisphere be provided, concentric with the other two, but smaller—suppose with a diameter ten inches across. Let the funnels which have been spoken of, and which lie between the outer surface and the primary surface, be made of some extensible material like indiarubber, their outer ends being fastened to the lenses and their inner ends to threads of glass the thickness of thin knitting-needles, and extending, as in fig. 3, from the

primary surface to the inner surface. To make it possible to do this, the glass hemisphere which we have used to represent the primary surface may now be removed; it is no longer required, since its position is sufficiently indicated by the points of junction of the indiarubber funnels and the glass

Fig. 3.
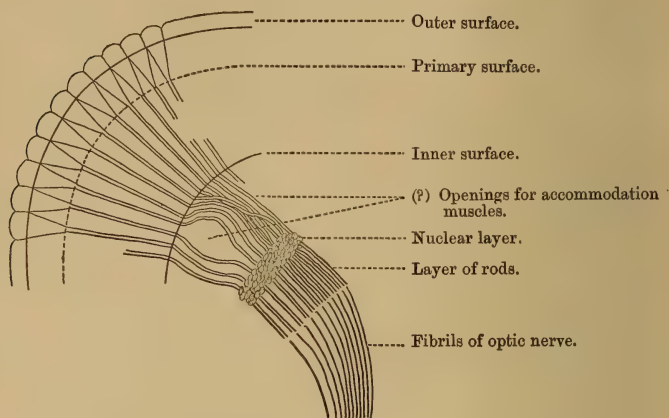
Section of an Insect's Eye (diagrammatic).

threads. The outer surface of our model, which carries the lenses, should be a stiff immovable arch, but the inner surface is to be made of some material which is capable of slightly contracting. If, after constructing the model in this way, its inner surface is made to shrink a little*, this will pull the glass threads inwards and elongate all the indiarubber cones. In this way the narrow ends of the cones are brought farther from their lenses, into the position where the image of a near object would be formed. The model now represents the insect's eye when accommodated for the vision of near objects.

In this model the image of the outer world is formed either at the primary surface or at the inner surface, for a speck of light falling on the upper end of one of the glass threads will travel lengthwise along the thread and emerge from its lower end, being kept from escaping laterally by

* A diminution of the radius of the inner surface of the model to the extent of about one millimetre would effect a sufficient range of accommodation. The motion in the insect's eye may need to be more than in proportion to this, since the filaments, as well as the funnels of its eye, are probably extensible, which is not the case in the model.

total reflexions. Now, it seems probable that something of this kind actually occurs in the insect's eye. In fact the apparatus corresponding to the rods and cones of our eyes seems, so far as I can make out, to be situated, not at the primary surface where the image is first formed, nor even at the inner surface where the image may be reproduced in the way described above, but in a deeper situation with which the inner surface communicates only through curved transparent threadlets. Each of these threadlets seems to have a thin transparent core, and if this core be of sufficiently highly refractive material, it would, although curved, be competent to carry the light forward by total internal reflexions, from the lower end of one of the glass threads to one of the pieces of the apparatus which corresponds to the layer of rods and cones in our eyes*.

It is, perhaps, worth observing that an eminently useful adjustment which we cannot effect seems to be possible in an insect's eye. In fact, the inner surface of our model might be drawn inwards more at one place than another ; and I am disposed to think that muscles, acting on the inner surface, are in the insect so disposed as to make this possible in its eye. Now this would effect an accommodation to the distances of objects which would differ in the different parts of the field of view†. Moreover, this result may be brought about in another way. The lenses and the funnels posterior to them vary in size from one part of the compound eye of a dragonfly to another, being largest in the position which I suppose to be about the middle of the eye, and gradually dwindling to about half this size near the margin‡. An equable contraction of the "inner surface" of such an eye would obviously effect a different accommodation in different

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* The light is probably carried forward most effectually where, as in the dragonfly, the cores are less than a micron in section, *i. e.* not much more than the wave-lengths of the light that has to traverse them. Light would adapt itself to the sinuosities of such filaments, like sound in a speaking-tube.

† In the sections of the eyes of dragonflies, which I have examined, the filaments from the funnels down to the "inner surface" are enclosed within a sheath of fibres and are straight, but immediately after passing through the inner surface they are each apparently enclosed within a tube, and grouped in bundles, between which are open spaces which may, perhaps, in the living insect have been occupied by muscles. Muscles, in this situation, would be competent to effect the optical adjustment spoken of in the text. (See fig. 3.)

‡ The increased aperture of the lenses towards the middle of a dragonfly's eye, and the diminished curvature of the stratum in which they lie, both conduce to make its vision more perfect towards the middle of its field of view ; and as this lies in the direction of the insect's flight, the arrangement must be of advantage to it in its pursuit of prey.

parts of the field of view. Accordingly, in one or other of these ways, or by a combination of them both, the insect may be able to adjust one part of its field of view for near objects, and other parts for more distant ones ; *e. g.*, a fly may be able to view distant objects around with the utmost distinctness of which its eye is capable, at the same time that it is closely scrutinizing the details of a lump of sugar and applying its proboscis rapidly to one minute crystal after another. As the adjustment which would enable it to do this would be of service to the insect, and as the construction of its eye admits of it, it seems likely that it is one for which provision has been actually made.

On a review of the whole subject we seem to have a satisfactory general insight into the process by which vision through compound eyes is carried on. Doubtless much detailed information of the minute anatomy of these interesting structures has been reached by microscopic anatomists ; but I am not acquainted with it, and have been obliged to rely on my own imperfect observations. It is, however, likely that, notwithstanding the diligence of microscopists, much still remains to be explored ; and this, I hope, may be followed up more intelligently if the general optical process is understood. It is on this account that I have endeavoured to trace it out, and especially because among my scientific friends there are to be found some of the most competent persons thoroughly to explore the whole of this interesting subject.

I have hitherto said nothing about vision through the isolated eyes with which insects are also furnished. They cannot, from the minuteness of their lenses, give them nearly so good vision of distant objects as man enjoys. And the limit is very possibly still more restricted by their being furnished with but a moderate number of rods and cones. It would be of interest to ascertain by observation whether this is so, and to collect such data as would enable us to estimate with tolerable exactness how far the imperfection goes.

[Note, *added February* 21.—It is not obvious why the apparatus of rods and cones in the human eye is nearly on as small a scale, and as closely packed over the rest of the retina as in the *fovea lutea*, since the amount of detail we can see in the corresponding parts of the field of view is immensely less. Possibly the line of the embryonic development of this layer may be such that it could not be evolved of the requisite minuteness in one part, without being made nearly as minute over the whole. The only other possible explanation seems to be that its being minute serves some other unknown purpose, as well as removing one of the three obstacles to our vision of small details.]

XXIX. *Notices respecting New Books.*

Theorie der Optischen Instrumente nach Abbe. *Von* Dr. Siegfried
Czapski. *Sonderdruck aus dem Handbuch der Physik von* A.
Winkelmann, Band II. 1893. Breslau, Ed. Trewendt; Williams
and Norgate.

THE subject of Geometrical Optics might with advantage be de-
fined so as to include all those parts of the theory of light and
optical instruments which can be treated by geometrical and formal
considerations, without detailed discussion of dynamical questions.
In strictness, of course, the Theory of Light is a branch of Dynamics;
but it is rather striking how completely the subject divides itself
into two distinct regions. The practically important part involves
but very slight recourse to dynamical treatment, while the specu-
lative part is almost wholly concerned with dynamical questions.
The title of Geometrical Optics to separate existence rests on
this fact; but it may fairly be urged that, in opposition to the
usual practice, the greater part of the subject of Diffraction and
Interference of light should be assigned to this branch of the
theory, on account both of its geometrical character and of its
importance for the working of optical instruments.

As ordinarily developed, the subject is a branch of Geometry
which is concerned with the reflexion and refraction of rays of light.
But if it is severed too much from the practical applications that
gave it birth, there is perhaps no department of mathematics
that can be made so repulsive. In matters of Pure Mathematics
the natural mode of progress is to adhere closely to the track of
symmetry and elegance; and there is no other canon of merit that
is applicable. But in the subjects that are cultivated more directly
for the sake of useful applications there is no choice of topics
allowed; and the aim must be to develop methods of investigation
that will satisfy the demand for mathematical elegance, and will
at the same time allow of an exact correlation between the mental
process and the natural phenomenon.

The book before us is a treatise on Geometrical Optics, compiled
from the point of view of the Theory of Optical Instruments. The
position which Dr. Czapski holds, in conjunction with Professor
Abbe, in relation to the famous manufacturing firm of Zeiss at
Jena, is a guarantee that the more technical information contained
in the work is exact and up to date. From the aspect of theory,
perhaps the most valuable feature of the book is the very copious
reference to the works of original writers; for to obtain a real
command of any department of a subject of wide practical ramifi-
cations, the consultation of text-books, however good, is but a poor
substitute for the assimilation of the ideas and points of view of
its original promoters. The treatise contains a very full account of
the topics which have been indicated above, with the exception of
the theory of Diffraction, of which the treatment is presumably left

to another department of the general undertaking of which this book forms a part. The phrase " nach Abbe " which occurs in the title is a little puzzling to non-German readers : in extending widely the capabilities of optical construction and manufacture, a very high degree of credit is due to Prof. Abbe and his collaborators at Jena ; but yet it seems strange to associate his name so markedly with the title of a theoretical treatise whose contents would appear for the most part familiar to many people who have possibly never heard of his work, and whose knowledge of Optics was acquired before his time.

From the nature of the book, as forming an article in an Encyclopedia of Physical Science, the subject is broken up somewhat into separate headings, with a view to facilitate reference. If ever the time comes for a final gathering together of the threads of this somewhat discursive subject into a compact form, it is to be hoped that much attention will be paid to the geometrical methods of discussion employed by the earlier English writers such as Robert Smith and Thomas Young, which amalgamate so easily with experimental requirements ; and that the capabilities of the Hamiltonian method of Action as a basis for the analytical part of the subject will be fully utilized.   J. L.

Anwendung der Quaternionen auf der Geometrie. *Von* Dr. P. MOLENBROEK.

THIS is the promised sequel to the *Theorie der Quaternionen* by the same author, which we reviewed in November 1891. In his preface Dr. Molenbroek replies to certain of our comments at that time.   He repudiates the description then given of his novel interpretation of $\sqrt{-1}$ as an operator.   Yet *his own* generalized description is in these words : " This definition shows that under the symbol $\sqrt{-1}a$ there are included not only an infinite number of arbitrary quaternions but also a similar number of right quotients [that is, versors] whose indices are all perpendicular to a."   And thus, we still must believe, the operator $\sqrt{-1}$ has the " singularly felicitous but hitherto unsuspected power of adjusting its axis so as to be perpendicular to any vector to which it may be applied !"

We had hoped to find in the present volume, which treats of geometrical applications, a further development of Dr. Molenbroek's pet creations—the *Vektorkreis*, the *Vektorkegel*, and the *Conisch Spaltender Quaternion*.   From plane triangles with their " circles " and " points," to curvature and geodetics, we find many good illustrations of the power and elegance of quaternions ; but of the conically spreading quaternion which transforms a vector into a conical sheet like a Japanese umbrella and then as with a fierce blast turns it inside out or in some other fashion de-axializes the original vector stem :—of this we find no mention.   Our disappointment is, however, more than balanced by the real quaternion character of the book as a whole.   A great many of the examples

are reproduced, with very slight changes of notation, from Professor Tait's well-known treatise, and, we are sorry to say, reproduced without acknowledgment. In his preface Dr. Molenbroek refers to Professor Tait only by way of criticism, accusing him of finding an integrating factor where none such can be. The truth is that quaternions give a solution where ordinary mathematics fail—although it would probably baffle even a Hamilton to give a *geometrical* interpretation of *log Uq*.

Occasionally Dr. Molenbroek advances along a path of his own, as, for example, in his *approach* to the quaternion equation of quadric surfaces. His transformation of the ordinary *Cartesian* equation (which is assumed) into quaternion form may well send a shiver down the back of a disciple of Hamilton.

Having neglected (as was pointed out in our former review) to discuss the operator ∇ in the *Theorie*, Dr. Molenbroek has to make a digression in the present volume so as to establish its elementary properties. In the preface he gives as an excuse for the former neglect the statement that Tait devotes only one line to ∇ in the theoretical part of his book. Still, Tait *has* it; and in the 3rd edition (1890) devotes four pages to it in the chapter on Differentation. But even in the very first edition (1867) of his treatise (in which no hard-and-fast line was drawn between the theoretical part and the applications) Tait gives ample evidence of the importance of ∇; and we still think that a more recent writer, wise in the accumulated experience of his predecessors, should have had something to say concerning the theory of this remarkable differentiating operator. Dr. Molenbroek himself employs it with effect in his discussion of partial differential equations. It plays a conspicuous *rôle* in the theory of orthogonal surfaces. It is pre-eminently the force-function operator. It is the heart of Green's theorem, the key-note of spherical harmonics. But we now learn on Dr. Molenbroek's authority that its value in physical applications is much over-rated (*sehr überschätzt*). We shall wait with interest his promised demonstration of this statement, which will probably be a unique feature of a succeeding volume. Meanwhile it is interesting to note that the last chapter of the present volume, which discusses with considerable elegance Hamilton's theory of rectilinear rays, ends with the equation, $S . \tau \nabla \tau = 0$.

It is satisfactory to find in Dr. Molenbroek an enthusiastic admirer of the quaternion and all that it involves. Adhering more or less closely to the methods and notation of Hamilton, he has made an honest endeavour to familiarize German reading students with the beauty and power of the system. We trust that his efforts will be rewarded and that in Leyden, at any rate, will grow up a school of Hamiltonian workers who will effectively help in developing the infinite resources of quaternions.

Physikalisches Praktikum, mit besonderer Berücksichtigung der physikalisch-chemischen Methoden. (*Practical Physics, with special reference to physico-chemical methods.*) By E. Wiedemann *and* H. Ebert. Second Edition, 1893. Vieweg und Sohn, Brunswick.

During the past year the subject of practical physics seems to have received an unusual amount of attention both in Germany and England. Some months ago we had occasion to notice a new work by Traube dealing with the methods of practical chemical physics, and the present volume bears a very similar title. Until quite recently Kohlrausch's classical text-book was almost universally adopted in German laboratories, but alterations in design of apparatus, changes in methods of teaching, and a necessity for the measurement of constants the importance of which was formerly unrecognized, have combined to make the work appear antiquated in a modern laboratory. The authors have treated the subject in a comprehensive manner as far as description of experiments is concerned; each section is introduced by an epitome of the theory of the experiments to be performed; this is followed by accounts of the experiments, apparatus and requisite manipulation, and when necessary the method of calculating results is indicated. The data of actual experiments are given as examples, and these show the degree of accuracy attainable. It would be an improvement if these data were stated in the way in which a student would be expected to write them down in his note-book, the method of entering results being one of the greatest difficulties experienced by the younger students in a laboratory. As they stand the quantities are merely designated by letters, of which the meanings can only be found by reference to the context.

As the work was written more especially for chemical students, the sections devoted to Electricity and Magnetism are not so complete as the rest of the book; for example the methods of measuring induction-coefficients and the capacity of a condenser are omitted. The rough determination of the specific inductive capacity of a dielectric, and of the resistance of a badly conducting liquid might, however, have been included with advantage.

The lists of apparatus required for each experiment form an excellent feature of the book, and will be of great service to the laboratory assistant. The illustrations are likewise good, especially those in colours, representing the solar spectrum, chromatic aberration, and grating spectra respectively. Indeed, the volume quite maintains the high standard which physicists have previously ascribed to the scientific work of its two authors.

<div align="right">James L. Howard.</div>

La Chaleur (Heat). By PIERRE DE HEEN, *Professor of Experimental Physics in the University of Liége.* Liége: Nierstrasz, 1894.

IN the somewhat remarkable preface to this work the author discusses the two methods of studying science by mere experiment and deduction therefrom, and by assumption of a theory which is afterwards put to the test of crucial experiment, respectively. It is only by the latter method that we succeed in acquiring a knowledge of the causes of things, which is the true aim of physical science. In the ordinary text-books of heat (and indeed of all branches of physics, except perhaps sound) the former method has been generally adopted; a miscellaneous collection of facts is given concerning expansion, the laws of gases, calorimetry, &c., and these lead to a higher analytical or mechanical development of the subject, but no theory is given to unite them into a connected system. Such a connecting link is first met with in the kinetic or molecular theory of gases, by which the behaviour of gases under various conditions of temperature and pressure is completely explained. By a suitable choice of temperature and pressure, however, a gas may be changed to liquid, or a liquid to solid, so that a similar theory must apply to all three states of matter. But as the molecules become crowded together the increasing complexity of their motions defies all calculation, although Van der Waals and others of the same school, to whose influence the present work is doubtless due, have achieved a certain amount of success in the case of liquids near their critical temperatures. Again, if we grant that the properties of liquids and solids are capable of explanation by molecular motion, it follows that such properties will be functions of the molecular weights of the substances. This conclusion has been verified in many cases in which a complete explanation is yet wanting.

In the volume before us heat is regarded as a molecular motion, and its chief phenomena are explained from this point of view as far as is possible in the present state of knowledge. The author assumes a knowledge of elementary phenomena, and occasionally borrows formulæ from thermodynamics, so that his work must be considered as an exposition of molecular physics rather than a text-book of heat. We have found several misprints in the book, notably in connexion with names of authors, for example Clairant, Peluj, Quinke, all of which might be corrected in a future edition.

JAMES L. HOWARD.

XXX. *Intelligence and Miscellaneous Articles.*

ON THE MAGNETIZATION OF SOFT IRON.   BY M. P. JOUBIN.

THE phenomena of magnetization have as yet only been represented by empirical and approximate expressions ; thus, for instance, the well-known formula of Fröhlich which is so frequently used does not show that the magnetic susceptibility passes through a maximum, a fact which is very important.

1. Let I be the intensity of magnetization, H the field, K the susceptibility, defined by the equation I = KH.   In order to find another relation between these three magnitudes we may, with Rowland, trace a curve by taking for coordinates not I and H, but I as ordinate, and K or 4πK as abscissæ.   To each value of K two values of I correspond, and the centre of each chord is on a right line very slightly inclined to the axis of abscissæ, and the angular coefficient of which is negative.   This curve is exactly a parabola (except near the axis of the ordinates) as Rowland has shown, who, however, represents it by a sinusoidal function. Thus it is that the equation

$$I = 660 - 0 \cdot 078\ 4\pi K \pm 14 \cdot 53 \sqrt{2336 - 4\pi K}$$

represents exactly the magnetic condition of an iron investigated by Bosanquet, as shown in the following table.   This example is taken at random among many others.

H.	4πK.	I. Calculated.	Observed.
0·2	629	12	10
0·5	753	25	30
1	1448	115	115
2	2281	375	363
5	1979	779	788
10	1301	1028	1035
20	744·5	1183	1183
50	323·3	1287	1286
100	170·5	1322	1356

2. The general aspect of these curves recalls in a striking manner the curves which give the densities of saturated fluids as a function of the temperature (MM. Cailletet and Mathias). To each value of the susceptibility (which replaces the temperature) correspond two values of the intensity of magnetization (or superficial density) which approach each other as K is increased, and merge into each other at the *critical point*.   The maximum

intensity I_m is nearly equal to three times the critical intensity I_c; in fact in the preceding example $I_c = 478$ and $I_m = 1400$, a third of which is 467. Now this property of ordinary fluids may be deduced from the equation of Van der Waals; we are thus led to inquire whether we may compare the magnetic properties to those of fluids.

3. Following Faraday, let us regard the field as occupied by tubes of force whose section σ at each point is inversely as the field, $\sigma H = 1$. In other words, instead of representing the intensity of the field by the number of lines of force per unit surface, let us define it by the section of unit tube. The coefficient K may then be written $I\sigma$; this is the quantity of magnetism contained in the section of unit tube, just as the temperature is the quantity of heat contained in unit volume of a gas.

Between the superficial density I *and the susceptibility* K *there is the same relation as between the cubical density* d *and the temperature* T *of a fluid*, a relation expressed by the formula of Van der Waals. Given a fluid obeying this law,

$$p = \frac{RT}{v - a} - \frac{c}{v^2}.$$

If it is gaseous and very far from its point of saturation, it virtually follows the law of Mariotte, and we may write $pv = RT$, from which is deduced the approximate law of its expansion,

$$c\,\frac{v - a}{av} = RT.$$

The expansion of unit volume is proportional to the absolute temperature. This expression leads us to Fröhlich's law.

Assume, in fact, that we can apply to magnetic phenomena the same equation, in which we shall replace a by $\dfrac{1}{I_m}$, T by K, and v by $\dfrac{1}{I}$; we shall have

$$p = \frac{RKH_m}{I_m - I} - c\,I^2.$$

Admitting, in conformity with a well-known demonstration, that the pressure exerted against the external medium on the surface is proportional to $I^2\sigma$, that is to say to KI, it will be seen that to write the equation $p = RKI$, is to express a law analogous to that of Mariotte. We deduce from this,

$$RI^2\sigma = \frac{RI^2\sigma I_m}{I_m - I} - cI^2,$$

from which

$$\sigma = \frac{1}{H} = \frac{c}{R} \frac{I_m - I}{H_m}.$$

This is Fröhlich's formula.

.Now this formula holds very well with feebly magnetic bodies ; we may from this conclude that in this case the pressure p is correctly valued. On the other hand, it does not agree with strongly magnetic bodies, for which the value of the pressure p is given by the formula of Van der Waals. From the known properties of this equation, the pressure corresponding to two values of I, corresponding to the same susceptibility K, is the same.

4. For a fluid, in proportion as the temperature T decreases the density of the saturated vapour decreases cotemporaneously with the tension ; at the temperature at which the density becomes null, the tension is null also. Thus the second part of the equation of Van der Waals vanishes, and we deduce from it the value of the density of the liquid under the pressure null of its saturated vapour.

Applying the same method to the example mentioned above, the parabola cuts the axis of abscissæ at the point $4\pi K = 516$; the corresponding value of I given by the equation of Van der Waals is $I = 1260$. The direct measurement on the parabola gives 1256. This is an almost absolute coincidence.

5. From this point the equation of Van der Waals can no longer represent the phenomenon, for the fluid can no longer exist in the liquid state ; a change of state takes place, and the representative curve changes suddenly. This is also the case with magnetism ; it is from this point that the curve is no longer parabolic. There is a change of state corresponding to the passage from the liquid to the solid state.

In fine, the phenomena of the magnetization of iron are analogous to those presented by a saturated fluid, and might be calculated by the same formulas ; I propose to try if we can find experimentally a *reduced equation* independent of the magnetized body.

Feebly magnetized bodies are subject to laws analogous to those of liquids at a distance from their point of saturation.—*Communicated by the Author*, from the *Comptes rendus*, Jan. 8, 1894.

ON THE EXPERIMENTAL INVESTIGATION OF THE ROTATIONAL COEFFICIENTS OF THERMAL CONDUCTIVITY. BY CH. SARET.

In the very amiable and indulgent notice which the *Archives de Genève* has published of my *Eléméns de Crystallographie physique*, M. Curie has proposed a method by which the existence

or absence of rotational coefficients of thermal conductivity in crystals may be ascertained in a simple manner.

I wish here to point out briefly the principle of an analogous method which I was led to try some time ago, and which, as I have subsequently learned, is identical with the method proposed by Boltzmann for the investigation of Hall's phenomenon.

If a point sufficiently distant from the edge of a thin crystallized plate be heated, the isothermal curves obtained by Senarmont's method are ellipses, whatever be the values of the coefficients of rotation.

If instead of working with a continuous plate the plate is split by a straight saw-cut in the direction of a radius from the centre of heating, the isothermal curves will be scarcely modified, and will shorten on each side of the slit if the coefficients of rotation are null, but will exhibit a break in the same region if the coefficients are not null. In this case the flow from the centre tends to follow a spiral line ; there should be an accumulation of heat on one of the edges of the slit and a falling off on the other.

The experiment may be made still more simply. Instead of sawing the plate it is sufficient to heat a point of the rectilinear edge. If the coefficients of rotation are not zero the isothermal line must undergo a spiral modification, and the distances at which it cuts the edge of the plate on the right and left of the point heated are not equal.

This method is not very certain : it is better to cut the plate by a saw-cut in two halves, which are then adjusted in a suitable support in their original position, leaving a slight interval between the two edges of the slit. By heating a point of this the spiral deformation should be separately produced on each piece, and the isothermal will present discontinuities in the opposite direction at the two points where it meets the slit.

I have tried these various methods on plates of gypsum ; in no case have I observed a discontinuity indicating an appreciable spiroidal deformation of the isotherms. I hope to pursue these experiments.

What we have said applies to *thin* plates perpendicular to the axis of rotation. It will be seen in like manner that on heating by Jannettaz's method a *point* in a face cut in an unlimited crystal, parallel to the axis of rotation, isotherms should be obtained which are not symmetrical in reference to that diameter which is parallel to this axis. The fact that this deformation has not hitherto been noticed appears to prove that the coefficients of rotation are always zero, or at any rate very small.—*Bibliothèque Universelle*, No. 4, 1893.

MECHANICAL ENERGY OF MOLECULES OF GASES.

To the Editors of the Philosophical Magazine.

GENTLEMEN,

Will you kindly allow me to ask, through the medium of your 'Philosophical Magazine,' whether there has ever been published a statement of the Amounts of *Mechanical* Energy of the Molecules of different Gases? and if so, where it is to be found?

If there has been no such publication, I beg leave to say that by calculating the mean molecular velocities per second at 0° C. of a considerable number of gases, simple and compound, from their molecular weights and the square roots of those weights (or of the specific gravities) in the usual manner, and multiplying the squares of those velocities by the molecular weights, I have observed that the resulting products are alike in amount, and therefore *the quantities of mechanical energy of the molecules of gases at the same temperature and pressure are equal.*

As it is possible that this general truth has been already observed and published (although during extensive reading on cognate subjects I have not seen it), I make the above statement with great diffidence.

I remain,

Yours truly,

Birmingham, Feb. 22, 1894.   GEORGE GORE.

Gas.	Sp. gr., or half molecular weight.	Square root of sp. gr.	Metres per second at 0° C.	Square of Molecular Velocity.	Amount of Mechanical Energy.
H	1·0	1·00	1842·6	3397175	3397175
H_2O	9·0	3·00	614·2	377242	3395175
NO_2	12·0	3·464	531·92	282939	3395268
N	14·0	3·74	492·67	242724	3398136
CO	14·0	3·74	492·67	242724	3398136
O	16·0	4·00	460·65	212198	3395168
F	19·0	4·358	422·617	178627	3393913
CO_2.........	22·0	4·69	392·87	154346	3395612
N_2O	22·0	4·69	392·87	154346	3395612
S	32·0	5·656	325·95	106243	3399789
ClO_2	33·8	5·813	316·98	100476	3396099
Cl	35·5	5·96	309·16	95580	3393090
HCl	36·5	6·04	305·06	93062	3396763
Cl_2O	43·5	6·595	279·39	78059	3395566
Cd	56·0	7·483	246·238	60634	3395504
P.............	62·0	7·874	234·01	54760	3395162
Se	79·5	8·916	206·66	42708	3395286
Br	80·0	8·938	206·15	42498	3399840
Hg	100·0	10·00	184·26	33951	3395174
I	127·0	11·27	163·495	26732	3394964
Te	129·0	11·357	162·24	26322	3395538
As	150·0	12·247	150·45	22635	3395280

XXXI. *On the Electricity of Drops.* By J. J. THOMSON,
*M.A., D.Sc., F.R.S., Cavendish Professor of Experimental
Physics, Cambridge*[*].

DROPS offer many advantages for the investigation of
electrical effects, especially of those which involve the
contact of dissimilar substances. Perhaps the greatest of these
advantages is that when the drops are formed they present a
perfectly clean surface to the gas by which they are sur-
rounded ; so that the conditions are much more definite than
they can be where the surfaces have been long exposed, and
have had time to get contaminated by dirt or coated with films
of gas of unknown composition.

The experiments described in this paper relate to the elec-
trical effects which occur when a drop of liquid falls on to a
plate already coated with a film of the same liquid. It has
been known for a long time that peculiar electric effects
occur at the feet of waterfalls : at such places the normal
distribution of the atmospheric electric potential is disturbed
in such a way as to indicate a distribution of negative elec-
tricity in the region at the foot of the fall. These effects cannot
be due to the waterfall acting like the falling drops in Lord
Kelvin's water-dropping electrophorus ; for they are found
to occur when the waterfalls are inside caves whose sides are

dripping with moisture, in which cases the water would be falling inside an equipotential surface.

The subject of the electrification produced by falling drops has been investigated by Lenard, who gives the results of his researches in a most interesting paper, entitled " Ueber die Electricität der Wasserfälle " (Wiedemann's *Annalen,* xlvi. p. 584). In this paper Lenard shows that when drops of distilled water fall on to a plate wetted by the water, the drops after striking the plate are positively electrified, while in the air around the place where the drops fall there is a distribution of negative electricity : that no electrical separation takes place until the drops strike against the plate : and that the electrical effect with drops of tap-water is very much less than with drops of distilled water.

Lenard attributes these effects to the formation of a double coating of electricity over the surface of the drop, the drop itself being coated with positive electricity, while in the air close to the surface of the drop there is a coating of negative electricity. When the drop strikes against the plate some of this external coating gets knocked off, leaving the drop with a preponderating positive charge, the corresponding negative charge going off into the air near to where the drop strikes against the plate.

Some phenomena I observed when an electric discharge was passing through an exhausted tube led me to the conclusion that bodies were covered with this double coating of electricity, but that its moment and even its sign depended very much on the nature of the gas surrounding the body on which the coating was situated. I was therefore led to make a series of experiments on the phenomena which accompany the splashing of drops, especially on the effect produced by altering the gas through which the drops fall and the liquid of which the drops are made.

The methods I used are very similar to those employed by Lenard; they are represented in figs. 1 and 2. The arrangement shown in fig. 1 was used to test the effect when different liquids fell through air; that in fig. 2 when the drops fell through gases other than air. A is an insulated funnel from which the drops fall : the substance of which this funnel was made was not found to produce any effect upon the results. I tried funnels of glass, lead, brass, iron, and silver : the mouth of this funnel dips below the top of a metal tube connected to earth. In fig. 2 the top of this tube is closed by a paraffin stopper through which the funnel passes. The drops fall on the plate B, and after striking against it fall into the vessel C, which is insulated and connected to the liquid in the funnel and to one pair of quadrants of the

Fig. 1.

Electrometer

A

To Earth

Fan.

B
C

To Electrometer

Fig. 2.

To Electrometer

A

← Gas

To Earth

To Earth

B

C

Gas

To Electrometer

2 A 2
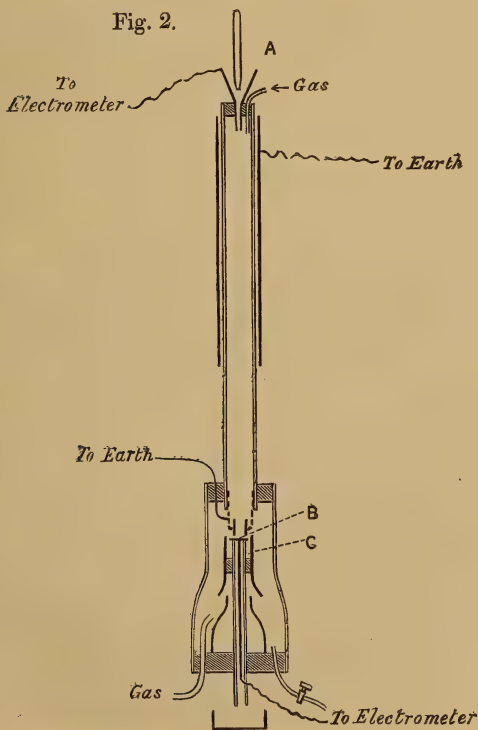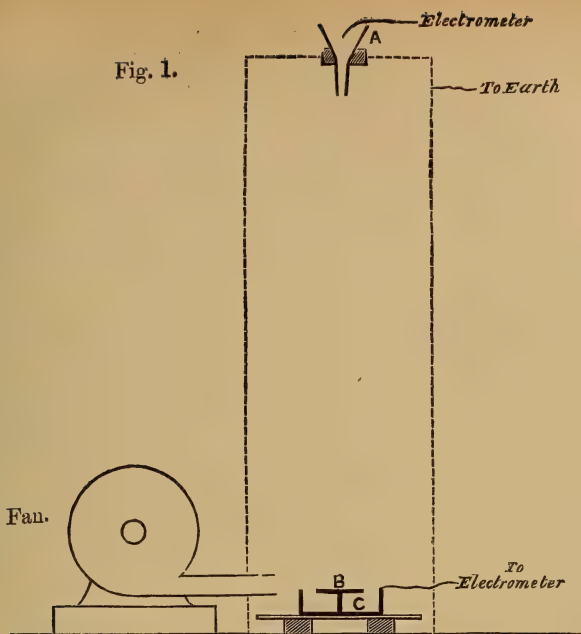
electrometer. The object of connecting the funnel to the vessel in which the drops are received is to eliminate the effect of any electrification that may be produced by the flow of the liquid through the funnel, or any electrical separation taking place when the drops fall from the spout of the funnel. It was found, however, by connecting the funnel by itself to the electrometer, that any effect of this kind was extremely small compared with those observed when both the funnel and receiver were connected with the electrometer. To prevent the electricity which goes into the air from charging the receiver, and thus neutralizing the opposite electrification given to the receiver from the drops, different methods were employed according as the drops fell through air, when the experiments could be made in the open, or through other gases, when the apparatus had to be enclosed in an air-tight vessel. In the first case the separation of the two electricities was effected by blowing a current of air across the plate on which the drops fell; the electrification in the air was by this means blown against a metal plate connected with the earth, and so discharged. The current of air was produced by a fan worked by a water-motor. This method could not be used when the apparatus had to be closed up so as to allow of gases other than air being used. In this case the electrification in the air was discharged by placing over the plate a piece of wire gauze connected with the earth : a hole was cut through the gauze to allow of the drops falling through without touching the gauze ; the gauze was separated from the plate by a distance only just great enough to allow the drops to fall into the receiver after rebounding from the plate without striking against the gauze. Plates of various kinds were tried, but I found, as Lenard observes, that the material of which the plate is made exerts no influence provided it is thoroughly wetted by the liquid which falls upon it. Irregularities occur if the plate is greasy, when the drops, instead of spreading over the plate, roll off it, still retaining their globular form.

With either of these pieces of apparatus the effect discovered by Lenard, that after striking against the plate drops of distilled water had a positive charge, could easily be observed.

The first variation of the experiment which I tried was to make the drops fall through water-vapour instead of air. For this experiment water was boiled for several hours in a vessel like that represented in fig. 2 until the steam had completely expelled the air : the water used for the drops had been well boiled so as to thoroughly expel the air from it. In this case no electrical separation whatever was observed, though when air was blown into the vessel the normal effect at once reappeared.

When the vessel was filled with hydrogen, the electrification of the drops was reversed: the drops, after striking against the plate, being negatively electrified, while there was a positive charge distributed through the hydrogen. Lenard found that the effect was considerably less in hydrogen than in air. If care is taken to get rid of all traces of air, the effect is not merely diminished but reversed.

This and the experiment previously described seem to indicate that the effect is due to chemical action. This view is confirmed by the very large effects produced by the addition of small quantities of various foreign substances to the water forming the drops.

The results of experiments made upon a considerable variety of substances are given below. In each case the deflexion given is that produced when 100 cubic centim. of the substance fall through the funnel. The deflexion is marked $+$ when it is in the same direction as that due to pure water falling through air.

Hydrochloric Acid.

Strength of Solution.				Deflexion.	Strength of Solution.				Deflexion.
Pure water..............				125+	$\cdot$2 c. c. of HCl made up to 100 c. c. with H_2O				0
$\cdot$2 c. c. of HCl in 10^4 c. c. of H_2O				100+					
$\cdot$4	,,	,,	,,	65+	$\cdot$4	,,	,,	,,	0
$\cdot$8	,,	,,	,,	45+	$\cdot$8	,,	,,	,,	2−
1$\cdot$6	,,	,,	,,	12+	1$\cdot$6	,,	,,	,,	3−
3$\cdot$2	,,	,,	,,	3+	3$\cdot$2	,,	,,	,,	0
6$\cdot$4	,,	,,	,,	0	6$\cdot$4	,,	,,	,,	2−
12$\cdot$8	,,	,,	,,	0	12$\cdot$8	,,	,,	,,	0
25$\cdot$0	,,	,,	,,	0	25$\cdot$0	,,	,,	,,	0
50$\cdot$0	,,	,,	,,	0	50$\cdot$0	,,	,,	,,	0

In this case any addition of the substance diminishes the electrical effect, and only requires a small quantity of HCl to make the solution neutral. When the solution has become neutral it remains so in spite of the addition of more acid. We shall see that other substances, such as zinc chloride, oxalic acid, &c., show the same peculiarity.

Sulphuric Acid.

Strength of Solution.					Deflexion.	Strength of Solution.					Deflexion.
Water					180+	1 c. c. of H_2SO_4 made up to 100 with H_2O ...					10−
$\cdot$2 c. c. of H_2SO_4 in 1000 c. c. of H_2O					40−						
$\cdot$7	,,	,,	,,	,,	30−	3	,,	,,	,,	,,	5−
1$\cdot$0	,,	,,	,,	,,	30−	10	,,	,,	,,	,,	10−
1$\cdot$7	,,	,,	,,	,,	35−	20	,,	,,	,,	,,	10−
3$\cdot$0	,,	,,	,,	,,	30−						
6$\cdot$0	,,	,,	,,	,,	30−						

A small amount of H_2SO_4 is thus sufficient to reverse the effect. Strong solutions are very nearly neutral.

Acetic Acid.

Strength of Solution.	Deflexion.	Strength of Solution.	Deflexion.
Water	190+	·2 c.c. of acid watered up to 100 c.c. ...... }	20−
·2 c.c. of acid in 10⁴ of water .... }	140+	·4 ,, ,, ,, ,,	35−
·8 ,, ,, ,, ,,	60+	·8 ,, ,, ,, ,,	45−
6·4 ,, ,, ,, ,,	35+	1·6 ,, ,, ,, ,,	55−
12·8 ,, ,, ,, ,,	5−	3·2 ,, ,, ,, ,,	25−
25·6 ,, ,, ,, ,,	10−	6·4 ,, ,, ,, ,,	30+
50·0 ,, ,, ,, ,,	15−	12·8 ,, ,, ,, ,,	100+

In this case the electric effect for moderately dilute solutions is opposite to that of water, while strong solutions give an effect of the same kind as water.

Phenol.

The phenol used was described as "granulated phenol." The solution called the standard solution below is made by taking ·2 cubic centim. of a saturated solution at 15° C. and mixing with it 100 cubic centim. of water.

Strength of Solution.	Deflexion.	Strength of Solution.	Deflexion.
Water	140+	·2 c.c. of saturated solution watered to 100 c.c. }	250+
·2 c.c. of standard solution in 100 c.c. of H_2O }	180+	·4 ,, ,, ,, ,,	520+
·8 ,, ,, ,, ,,	170+	·8 ,, ,, ,, ,,	730+
3·2 ,, ,, ,, ,,	210+	1·6 ,, ,, ,, ,,	850+
50·0 ,, ,, ,, ,,	190+	3·2 ,, ,, ,, ,,	920+
		6·4 ,, ,, ,, ,,	870+
		12·8 ,, ,, ,, ,,	270+
		25·0 ,, ,, ,, ,,	5−
		50·0 ,, ,, ,, ,,	25−

The effects produced by a small quantity of phenol are very striking, increasing the deflexion nearly sevenfold. On the other hand, a strong solution is nearly neutral.

Hydriodic Acid.

The standard solution contained ·2 cubic centim. of HI in 100 cubic centim. of water.

Strength of Solution.	Deflexion.
Water	275+
·2 c.c. of standard solution in 100 c.c. of water......	280+
·4 ,, ,, ,, ,, ,, ...	180+
·8 ,, ,, ,, ,, ,, ...	50+
1·6 ,, ,, ,, ,, ,, ...	30+
3·2 ,, ,, ,, ,, ,, ...	0
6·4 ,, ,, ,, ,, ,, ...	3−
·2·8 ,, ,, ,, ,, ,, ...	10−
·2 c.c. of acid watered up to 100 c.c.	10−
·4 ,, ,, ,, ,, ...	10−

The hydriodic acid thus diminishes the water effect : the stronger solutions are nearly neutral.

Oxalic Acid.

The standard solution contained 1 centigramme of acid in 100 cubic centim. of water.

Strength of Solution.				Deflexion.	Strength of Solution.				Deflexion.
Water				255 +	·01 grm. of acid in 100 c. c. of water				20 +
·2 c. c. of standard solution in 100 c. c. of water				280 +	·02 ,, ,, ,, ,,				10 +
3·2	,, ,, ,, ,,			190 +	·04 ,, ,, ,, ,,				0
6·4	,, ,, ,, ,,			110 +	·16 ,, ,, ,, ,,				0
25·0	,, ,, ,, ,,			60 +	1·25 grms. ,, ,, ,,				0
50·0	,, ,, ,, ,,			40 +	5·0 ,, ,, ,, ,,				0

Tartaric and formic acid gave very similar results.

Zinc Chloride.

Strength of Solution.					Deflexion.
Water					170 +
·0017 gramme of $ZnCl_2$ in 100 c. c. of H_2O					150 +
·0136	,,	,,	,,	,, ...	60 +
·085	,,	,,	,,	,, ...	15 +
·17	,,	,,	,,	,, ...	5 +
1·36 grammes	,,	,,	,,	,, ...	0
10·8	,,	,,	,,	,, ...	0
85·0	,,	,,	,,	,, ...	0

Thus zinc chloride behaves in the same way as hydrochloric and the other acids.

Chromium Trioxide.

Strength of Solution.				Deflexion.	Strength of Solution.				Deflexion.
Water				30 +	·01 gramme of salt in 100 c. c.				140 −
·00016 gramme of salt in 100 c. c.				15 +	·04 ,, ,, ,,				210 −
·00064	,, ,,	,,		15 −	·16 ,, ,, ,,				225 −
·00128	,, ,,	,,		50 −	1·25 grms. ,, ,,				270 −
·00256	,, ,,	,,		85 −	2·5 ,, ,, ,,				240 −
·005	,, ,,	,,		110 −	5·0 ,, ,, ,,				190 −

Thus chromium trioxide reverses the electrification on the drop, producing a very large negative electrification on the drops.

Effects similar to those produced by chromium trioxide are also produced by hydrogen peroxide.

Potassium Iodide.

Strength of Solution.	Deflexion.
Water	390+
·04 gramme of KI in 100 c.c. of H_2O	70−
·12 „ „ „ „	100−
·32 „ „ „ „	110−

A similar reversal to that shown by chromium trioxide.

Potassium Permanganate.

Strength of Solution.	Deflexion.
Water	230+
·025 gramme of permanganate in 100 c.c. of H_2O ...	145−

Thus the addition of potassium permanganate produces a reversal of the electrification.

Though the addition of mineral salts and acids produces a very decided effect on the electrification, this effect is not nearly so large as that produced by very dilute solutions of organic compounds. We have seen an instance of this already in the case of phenol, which produced an enormous increase in the electrification of the drops. An equally remarkable effect is produced by methyl violet, but in this case the electrification of the drop is reversed: the merest trace of methyl violet is sufficient to reverse the electrification, and in fact a weak solution is much more effective than a strong one, a very strong solution being almost neutral. The effect of methyl violet is so great that when a funnel has been used for this substance, many litres of water have to be run through it before distilled water when running through it gives the normal effect. The following measurements show the large effects produced by small quantities of methyl violet: the standard solution mentioned below was distinctly, though not deeply, coloured.

Methyl Violet.

Strength of Solution.	Deflexion.
Water	350+
2 drops of standard solution in 100 c.c. of H_2O ...	450−
·2 c.c. „ „ „ „ „ ...	370−
·4 „ „ „ „ „ „ ...	370−
1·0 „ „ „ „ „ „ ...	280−
10·0 „ „ „ „ „ „ ...	210−
40·0 „ „ „ „ „ „ ...	100−

Rosaniline also produces an effect of the same character as methyl violet, though not quite to the same extent: thus, when the distilled water gave a deflexion 200+, a weak solution of rosaniline gave a deflexion 370−; stronger solutions

produced much smaller effects. The effect of adding a small quantity of rosaniline to water could be detected by the alteration produced in the deflexion of the electrometer before any colour was appreciable.

Fluorescene and eosine produce very marked effects, but of the opposite kind to those due to methyl violet and rosaniline, *i. e.*, instead of reversing the water effect, they increase it. Thus when water gave a deflexion 280 +, a weak solution of fluorescene gave a deflexion 700 + ; and when water gave a deflexion 200 +, a weak solution of eosine gave a deflexion 370 +. As the solutions of eosine and fluorescene increase in strength the electrical effects get smaller, until with very strong solutions a small negative deflexion is obtained in both cases.

When a solution has become electrically neutral, *i. e.* when the drops do not produce any deflexion of the electrometer, the addition of other reagents seems to produce very little effect. Thus to 100 c. c. of a neutral eosine solution I added 12 drops of a rosaniline solution, and the solution still remained neutral, though the addition of the same quantity of the rosaniline solution to 100 c. c. of distilled water produced a change in the deflexion of the electrometer of 400 scale-divisions.

The effect produced by any reagent depends to a very large extent on the solvent in which it is dissolved. I tried the effect of dissolving rosaniline, methyl violet, fluorescene, eosine, and phenol in absolute alcohol as well as in methylated spirit : the electrical effects, however, were small, in no way comparable to the enormous effects produced by these substances when dissolved in water.

Isomeric Substances.

Dr. Ruhemann was kind enough to supply me with samples of the three isomeric substances hydroquinone, pyrocatechin, and resorcin. The solutions of these were of the same strength, ·5 gramme of the salt being dissolved in a litre of water. The results were as follows :—

Substance.	Deflexion.
Water	210 +
Pyrocatechin	205 +
Resorcin	205 +
Hydroquinone	255 +

Thus the hydroquinone is the only one of the three which produces any appreciable effect on the electricity produced by the drops.

Effect of Temperature upon the Amount of Electricity produced.

The electrification produced by drops of distilled water increases as the temperature increases; this is shown by the following measurements made at different temperatures:—

Temperature.	Deflexion.
15° C.	230+
75° C.	390+
95° C.	420+

The effect of temperature upon a solution of rosaniline is very remarkable. At first increase of temperature produces an increase in the electrification, but on increasing the temperature still further the electrification diminishes and finally changes sign. The deflexions due to a rosaniline solution are given in the following table:—

Temperature.	Deflexion.
15° C.	180−
70° C.	260−
75° C.	120−
90° C.	20+
95° C.	40+

Effect of Altering the Gas surrounding the Drops.

I have already alluded to the reversal of the electrification of drops of distilled water which takes place when hydrogen is substituted for air. If in place of distilled water we use dilute solutions of different substances, we find that the effect of substituting hydrogen for air depends very much upon the nature of the solution. Solutions such as those of phenol, pyrogallic acid, fluorescene, whose drops are electrified in the same way as those of distilled water, are affected by hydrogen in the same way as the drops of water are affected; *i. e.*, the positive electrification which the drop possesses in air is in hydrogen exchanged for a small negative electrification. On the other hand, the effect of substituting hydrogen for air in the case of substances like methyl violet, rosaniline, potassium permanganate, whose drops show a negative electrification in air, is to increase this negative electrification, and the deflexion of the electrometer is greater when the drops fall through hydrogen than when they fall through air.

This is shown by the following table :—

Substance.	Deflexion when drops fall through air.	Deflexion when drops fall through coal-gas.	Deflexion when drops fall through hydrogen.
Water	230+	95+	25—
Fluorescene in water	110+	8+	125—
Eosine in water	200+	200+	35+
Rosaniline in water	360—	360—	395—
Methyl violet	325—	330—	580—
Potassium permanganate	70—	133—	
Phenol in water	310+	...	10—
Absolute alcohol............	40+	...	150—
Methyl violet in alcohol...	15—	...	130—
Phenol in alcohol	5—	...	70—

When drops fall through sulphuretted hydrogen, the deflexion of the electrometer is very small whatever be the nature of the drop. I am inclined to attribute this to the absorption of the gas by the water of the solution; the drops absorb so much gas that they may be regarded as pretty strong solutions of sulphuretted hydrogen, and it is consistent with what we have seen of the behaviour of solutions of salts or acids that a strong solution should be electrically neutral. This explanation is supported by the fact that, whereas to get the hydrogen effect it is necessary to take the greatest pains to exclude the air, we can get the effect produced by sulphuretted hydrogen when a good deal of residual air remains in the gas surrounding the drops. I also found that when water in which sulphuretted hydrogen had been dissolved fell in drops through air, no electrical effect was produced.

When solutions of rosaniline and methyl violet fell through chlorine, the drops had a slight positive charge; the same drops when falling through air or hydrogen had a negative charge: the solutions were quite bleached by the chlorine. When chlorine water falls through chlorine, no electrification is produced.

Discussion of the Results.

The preceding experiments show that the electrification developed by the drop depends (1) on the nature of the gas surrounding the drop ; (2) on the nature of the drop itself. On the drop side of the surface of separation of the drop and the gas there is a coating of one kind of electricity

close to this, but in the gas there is a coating of the opposite kind of electricity. The quantity of positive electricity on one coating is equal to the quantity of negative electricity on the other. With an electro-negative gas like oxygen, the negative layer of this double coating of electricity is in the oxygen when the drop is formed of distilled water, or of a solution of readily oxidizable substances, such as pyrogallic acid, or phenol, or of dilute solutions of eosine and fluorescene. If the oxygen is replaced by the electro-positive gas hydrogen, then the positive layer of the coating is in the hydrogen, not only for the drops mentioned above but also for all the drops I have tried, with the exception of mercury. This substance I have always found to be positively electrified whether it fell through air or hydrogen. I hope, however, to test this point further by trying still purer hydrogen. When the drops are solutions of strongly oxidizing substances, such as chromium trioxide, hydrogen peroxide, potassium permanganate, or weak solutions of certain dyes, such as rosaniline or methyl violet, the positive coating seems always to be in the gas, whether this be oxygen or hydrogen; the electrical effect is, however, greater in the latter case than in the former. With chlorine, however, the negative coating seems always to be in the gas. These results, together with the fact that when water falls through its own vapour, or when chlorine water falls through chlorine, no electrical effect is produced, seem clearly to indicate that the electrification owes its origin to chemical processes. In fact the phenomena point to the conclusion that over the surface of the drop a substance is formed which is in a state intermediate between that of complete chemical combination and complete separation between the gas and the liquid forming the drop : a state in which the constituents have electrical charges of the same sign as in actual chemical compounds, but in which the connexion between the constituents is so loose that they can easily be shaken apart. We must regard this state rather as an attempt or tendency towards chemical combination than the formation of a definite stable chemical compound, for we could not suppose that such a compound would be split up when the drop struck against a wet plate.

The greatest electrical effect will occur when there is a tendency towards chemical combination, though not of sufficient intensity to result, in the time taken by the drop to fall from the funnel to the plate, in the formation of a definite chemical compound. The influence of this tendency in increasing the electrical effect is shown by the experiments on weak solutions of the three isomeric substances, resorcin,

pyrocatechin, and hydroquinone. Of these the last was the only one that increased the electrical effect of the drops beyond that due to the water in which it was dissolved, and hydroquinone is the only one of the three which has any tendency to combine with oxygen.

The difference between the magnitude of the changes produced in the electrical effects when the same substances are dissolved in water and alcohol, shows that the quasi-chemical action which produces the electrification is greatly influenced, if not altogether determined, by the solvent. Thus the small effect produced when phenol is dissolved in alcohol compared with that produced when it is dissolved in water, shows that phenol by itself does not produce much electrical effect, but that when a small quantity of it is dissolved in water, it is put into a state in which it can exert a chemical action which is accompanied by a vigorous electrical effect. The addition of a small quantity of a salt or acid to the water seems to deprive the water of the power of putting phenol into this state. Thus I made a weak solution of sodium chloride which was electrical neutral, and to this added a small quantity of phenol : the solution remained electrically neutral, the drops giving rise to no electrification. The phenol in this case produced no effect, though the same quantity of phenol, when added to pure distilled water, more than doubled the electric effect due to the water.

The vigorous electric action of some organic substances is very striking, especially the fact that very dilute solutions produce much larger effects than strong ones : in this they resemble inorganic substances, as strong solutions of all the substances I have tried produce very little electrification. This could be accounted for to some extent by the better electrical conductivity of the strong solutions, because this would make it more difficult for the electricity of opposite sign to that on the drop to escape into the air, as it would more readily get into the surrounding fluid : just as Lenard found that the electrification was diminished when the thickness of the layer of water into which the drops fell was increased. We cannot, however, attribute the whole, or even the greater part of the diminution due to strong solutions to this cause, since the diminution produced by increasing the strength of the solution is far greater than the increase in its conductivity.

The conclusion to which I have been led by the study of those drops is that distilled water is a substance which is far from being chemically saturated and inert, but that, on the contrary, it can by its chemical action set up those chemical

changes in the gas by which it is surrounded or in substances dissolved in it which give rise to the electrification. As, however, the quantity of substance dissolved in the gas is increased the mixture becomes more nearly chemically saturated or neutral, and more incapable of producing the requisite chemical change in the surrounding gas, or of putting the substance dissolved in it into a state in which it is chemically active. At a certain stage the diminution in the chemical activity of the water produced by the addition of more of the substance, more than counterbalances the effect due to the increase in the number of molecules of the substance. When this stage is reached, any increase in the strength of the solution will diminish the electrical effect. We may put this reasoning in a mathematical form : Suppose that A is the measure of the electric effect due to the action of the distilled water on the air, and that when m gramme molecules of a salt are dissolved in a litre of water, the mixture becomes more nearly chemically neutral, and its power of originating the chemical change which produces the electrical double layer is enfeebled, so that the electric effect is now only equal to $A\epsilon^{-\beta m}$, where β is some constant. Suppose, too, that the distilled water could put a fraction B of the molecules of the salt into the condition in which they are able to produce the chemical changes which lead to electrification, but that the solution is only capable of putting the fraction $B\epsilon^{-\gamma m}$ into this state. Suppose, too, that each molecule in this state produces an electric effect represented by C/B. On these suppositions the electric effect of the drops, which is the sum of the effects of the water and the salt, will be proportional to

$$A\epsilon^{-\beta m} + Cm\epsilon^{-\gamma m}.$$

If we represent this relation by a curve in which the ordinate represents the electric effect, the abscissa the strength of the solution, we get the curves of the type α, β, γ according as C is of the same sign as A, of the opposite sign, or zero (fig. 3).

These curves represent the general behaviour of the substances I have examined. Curves of the type α represent the behaviour of solutions of phenol, eosine, fluorescene ; curves of the type β that of solutions of potassium permanganate, chromium trioxide, hydrogen peroxide, rosaniline, and methyl violet ; and curves of the type γ that of solutions of zinc chloride, hydrochloric and hydriodic acids.

The measurement of the electrification developed by the drops does not enable us to find the potential difference between the drop and the surrounding gas ; it only shows that this difference is finite and enables us to determine its

sign.   Other considerations show, however, that this differ-
ence cannot amount to anything like a volt, for otherwise the
difference between the surface-tension of distilled water and a
weak electrical neutral solution of, say, sodium chloride would

Fig. 3.
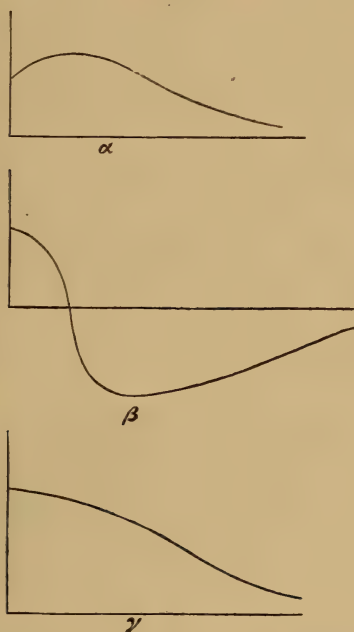
be far greater than it is.   Let V be the difference of potential
between the drop and the air, S the area of the surface of the
drop, t the distance between the two coatings of electricity;
then the two coatings may be regarded as the charged plates
of the condenser, whose potential energy is

$$\frac{1}{2}\frac{SV^2}{4\pi t};$$

or, if Q is the charge on either coating,

$$2\pi t\frac{Q^2}{S}.$$

The existence of this double coating will thus diminish the
apparent surface-tension by

$$2\pi t\frac{Q^2}{S^2},$$

which is equal to

$$\frac{V^2}{8\pi t}.$$

If V is equal to 1 volt and t to 10^{-8}, this is about 44. Thus, if we take the cases of distilled water and an electrically neutral solution of sodium chloride, which is an exceedingly weak solution; then, if there were a difference of potential of 1 volt between distilled water and air, the apparent surface-tension of the salt-solution would exceed that of pure water by about 44. The effect of the electrification on the surface-tension is proportional to the square of the potential-difference. Thus for a potential-difference of one tenth of a volt the difference between the surface-tension of distilled water and a weak salt-solution from this cause would only be about ·44. It is doubtful whether the measurements of surface-tension could be trusted to detect differences as small as this; so that all we can infer from the observations on the surface-tension of solutions is that the difference of potential between distilled water and air cannot be much greater than one tenth of a volt.

There seems no reason for limiting the possession of this double coating to liquids. It is possessed by liquids of the most diverse characters, as is shown by the electrification developed by drops of water, mercury, molten metals, turpentine, &c. If, however, we suppose that solids possess such a coating, it is evident that the rubbing off of part of one of these coatings when two solids are rubbed together would show itself as electricity developed by friction. Indeed it seems quite possible that a large part, if not the whole, of the electricity developed by friction may be due to this cause.

Another phenomenon in which I am inclined to think this double layer of electrification over the surface of bodies plays an important part, is the electrification of metals and fluorescent liquids when exposed to the influence of ultra-violet light. These substances under such circumstances acquire a charge of positive electricity, the negative electricity going to the air. Now in mercury and molten liquids and solutions of the fluorescent substances eosine and fluorescene the positive layer of the double coating is next the metal or liquid, the negative layer next the air. It seems quite possible that when there is intense reflexion of light from the surface of these substances, the outer coating may get partially dissipated, leaving the metal or liquid with a positive charge. A solution of rosaniline also shows the same effect when exposed to ultra-violet light, though the electrification of its drops is at low temperatures of the opposite sign to that of

solutions of eosine or fluorescene. We have seen, however, that at high temperatures the electrification of a solution of rosaniline changes its sign ; and the state of the outer layers when exposed to intense light may very well be more analogous to that of the liquid at a high temperature than at a low one.

Again, the formation of large drops of water by the impact of smaller ones is analogous to the splashing of the water-drops against a wet surface, and is likely to give rise to analogous electrical effects on a smaller scale. If this is so, the large drops of rain which frequently accompany thunderstorms may be to some extent rather the cause than the effect of the storm. I believe that this has been suggested by Sir G. G. Stokes.

The difference in the behaviour of different gases with reference to the two electricities is very conspicuous in these experiments, oxygen and chlorine acquiring a charge of negative electricity when under the same circumstances hydrogen acquires a positive charge. This suggests that the energy possessed by an atom of hydrogen, for example, when charged with a unit of positive electricity is not the same as that possessed by the same atom when charged with a unit of negative electricity ; or, as v. Helmholtz expresses it, the atoms of various substances attract the two electricities with different intensities. If the atoms possess this property they will tend to acquire definite atomic charges, and thus tend to have a definite valency. We can see this if we remember that the likelihood of the formation of a chemical compound is conditioned by the changes in the energy which accompany the formation of the compound. We shall for the sake of clearness confine our attention to the changes which go on in the potential energy. Any chemical change will tend to go on if it is accompanied by a decrease in the potential energy, and will tend to be reversed if it is accompanied by an increase in that energy. Let us consider the case of an element the potential energy of whose atom is diminished by Q when one unit of positive electricity is communicated to it. If C is the electric capacity of the atom, then, when the atom has a charge of n units of positive electricity, its electric potential energy is

$$\frac{1}{2} \frac{n^2}{C} - Qn.$$

Thus the charging of the atom will result in a diminution of the potential energy until, supposing the unit of electricity to be indivisible, the charge on the atom is the integer just less than CQ : when the charge exceeds this an increase in

the charge will be accompanied by an increase in the potential energy. Thus there will, on account of the property which may be expressed as a specific attraction of the atom for electricity, be a tendency for the atom to acquire the definite charge CQ. If, however, the atom has a definite charge it has a definite valency. We must remember, however, that when chemical changes are going on, the charges gained by one atom are lost by another; and it is the total change in the potential energy which determines whether the change shall go forwards or backwards. Thus in some cases we may have an atom charged to an extent which involved an increase in its potential energy, because the abnormal charging of this atom may have involved such a decrease in the potential energy of some other atom as to more than compensate for the increase in that of the atom under consideration. In this case the atom would not have its normal valency.

It would appear that if the atoms possess this specific attraction for the two electricities, a large rotating body ought to produce a magnetic field. For consider a substance the atoms in whose molecules attract the two electricities with different intensities, and suppose, for example, that the electro-negative component is the more energetic of the two: then, in consequence of the uncompensated attraction of this atom for a negative charge, there will be in the neighbourhood of the atom an electric intensity in the same direction as that which would exist if the atom had a positive charge. This effect may be inappreciable at finite distance from the molecule and produce no external electrostatic effects. When, however, the molecule is set in motion, the specific attraction of the molecule would make the positive electric tubes move in a different way to the negative ones. This differential motion of the tubes would produce a magnetic field of the same general character as that due to a positive charge moving in the direction of the molecule. In the case of a rotating sphere the maximum magnetic force at the surface would be proportional to ωa^2, where ω is the angular velocity of rotation, and a the radius of the sphere. If we take the earth's magnetic force as an index of the superior limit of the magnetic force due to a rotating sphere of the size of the earth, we find that the magnetic force due to a sphere 1 foot in radius rotating 100 times a second would not exceed more than about one hundred millionth part of the earth's magnetic force.

I have much pleasure in thanking my assistant, Mr. F. Everett, for the assistance he has given me in these experiments.

XXXII. *The Densities of Solutions of Soda and Potash.* *By* Spencer Umfreville Pickering, *F.R.S.*[*]

IT is somewhat remarkable that there exist no modern or exact determinations of the densities of solutions of soda or potash. Berthelot, it is true, made series of observations with both substances, but his results have no pretensions to accuracy, the values being given to the third decimal place only, and applying to temperatures varying from 10° to 15°. The tables which are generally reproduced in text-books, as well as in the works of Schiff and of Gerlach on densities, are those which Tünnermann constructed as far back as 1827. These tables are based on half a dozen determinations at most, and on a theory which can scarcely be accepted at the present day ; they are fairly voluminous, and as Tünnermann calculated the values for percentage strengths not expressed by round numbers, they seem to have been generally accepted as experimental instead of calculated values. They show errors extending up to a unit in the second decimal place, and when plotted out give figures bearing very little resemblance to the true ones. Dalton also made some determinations ('Elements,' ii. p. 315 [†]), and possibly also Richter (*Stöchiometrie*, iii. p. 332 [†]), but as I have failed in procuring his work (or Dalton's either) I am uncertain whether they were original determinations or not. In any case determinations of such a date could only be roughly approximate.

Apart from the desirability for practical purposes of having accurate tables of the densities of such familiar substances as soda and potash, there were questions of theoretical importance which induced me to investigate their solutions. My work on Sulphuric Acid (Chem. Soc. Trans. 1890, pp. 64, 331) had indicated the existence of numerous hydrates in solution, but beyond the indications afforded by the changes of curvature themselves there was very little independent evidence as to the particular hydrates indicated, one only had been known to exist in the solid condition, and one other was subsequently isolated. But in the case of soda, my recent work (Chem. Soc. Trans. 1893, p. 890) has shown that the hydrates which can be crystallized from moderately strong

[*] Communicated by the Author.

[†] These references are taken from Watts's 'Dictionary of Chemistry,' v. p. 339.

solutions are very numerous, and if it is established that the properties of the solutions show changes of curvature at points corresponding to these isolated hydrates, we shall have further evidence of a very strong character in favour of the reality of these changes, and of the view that they indicate the existence of hydrates in solution.

The Determinations.

The soda used was made from sodium, and the potash was purified by crystallization from alcohol. The lumps were first washed in well-boiled water to remove any adhering carbonate, and were then dissolved to form solutions nearly saturated at ordinary temperatures, and filtered through glass-wool. These strong solutions were subsequently diluted to the required strengths by the addition of accurately weighed quantities of water. The solutions were made up twelve to twenty-four hours before their densities were determined, specially stopped bottles of common white glass being used for holding them during this time. The same solution was never used twice. In spite of every precaution the solutions could not be obtained entirely free from carbonate : the presence of a little carbonate, however, would have no appreciable effect on the relative accuracy of consecutive observations, which is the chief consideration in the present work.

The strength of the stock solutions was determined by titration, and was probably correct to 0·05 per cent. of the total alkali present. The relative strength of the consecutive solutions is dependent only on the balance error in diluting them, and is therefore represented by a much smaller quantity.

The density-determinations were made in a precisely similar manner as in the case of sulphuric acid, the temperature, however, being $15° \pm ·01$. The various determinations of consecutive strengths were not always made consecutively. The results with soda, for instance, were made in five or six different series, each extending throughout the whole range of strengths investigated, and any changes which are noticed cannot, therefore, be explained away by the suggestion of there being a certain error affecting a certain day's work, and not affecting that of another day.

Examination of the Results with Soda.

The results with soda are given in Table I. A considerable number of the observations were repeated with solutions of nearly the same strengths, and the means deduced from these duplicates have been used for plotting purposes. From this cause the mean experimental error is less than it was in the case of my determinations with sulphuric acid (·000011, see Phil. Mag. xxxiii. p. 136). The graphic method—which is based on measuring the errors of every two alternate points as compared with arcs of circles drawn through three other alternate points (*Ber. d. deutsch. chem. Gesell.* xxiv. p. 3332, xxv. p. 1100)—gave ·00000734 when applied to the whole series of values; but if there are any breaks in the figure it is obvious that the arcs should not be applied so as to bridge over a break, as the errors in its neighbourhood would thereby be made to appear larger than they really are. When applied so as to avoid bridging over the breaks which the figure appears to show, the mean error was found to be ·00000631 ; and, as the following examination sufficiently establishes the reality of these breaks, this value for the error has been accepted. The general character of the results, however, it must be noted, would not be altered if the higher estimate were taken.

The densities themselves, when plotted against percentage composition, form a figure which shows that throughout they increase with the strength at a decreasing rate. In order that a scale might be adopted sufficiently open to give the experimental error a visible magnitude, the differences between the densities and a straight line (third column), or between the densities and a simple parabola (fourth column), have been used for the examination. The values given by the former are preferable for determining the position of any breaks, owing to the simpler character of the figure formed by them ; those given by the latter are preferable for the estimation of the errors of the drawings, owing to the more open scale which can be used in plotting them. These latter values are shown in the diagram, though the scale which has necessarily been adopted there is too restricted for purposes other than those of illustration.

A glance at this figure will be sufficient to show that they cannot be expressed by any single bent-lath curve ; and a more careful examination of them with the lath indicates the probable existence of as many as eight changes of curvature, as shown in the diagram (p. 363). When the apparent errors of the points according to such a drawing are measured, the results

given in column A of Table II. are obtained *. In this case the total error is 1·6 times the known experimental error, but this comparatively small excess above what it should be is, as will be seen, due entirely to the magnitude of the e_2 error, and might be caused by even one experimental point showing an accidentally large error. Very little weight ought therefore to be attached to it, and the drawing cannot be regarded otherwise than as agreeing very closely with the known experimental error ; indeed, the mean apparent error of the points (e_1) agrees almost absolutely with the experimental error—·00000627 against ·00000631.

If the breaks shown by this drawing have no real existence, and if it is merely by some strange chance that the drawing has been made in precisely the right number of sections to produce this remarkable concordance between the apparent error of the points and the known experimental error, we ought to get a similar concordance with any other drawing of a similar degree of complexity independent of the particular positions at which the breaks are made to come. But this is not so. The results given in columns B show that if the breaks are made to come at points intermediate between those in the previous drawing, the apparent error is increased from 1·6 to 6·6 times the experimental error, every one of the factors which make up the total error being in excess of what it should be. Therefore the breaks shown by the A drawing must be in reality singular points in the figure.

In the B drawing, it must be noticed, it is necessary for the sake of fair comparison to omit the half sections which are left at each extremity of the figure, and to deal only with the remaining eight sections which are comparable in length, and in the number of experimental points on them, with the nine sections in the A drawing. It will also be noticed that the sums of the + and − errors are not very equally balanced ; but in this case, as in some others which have been investigated (see, for instance, *Ber.* xxv. p. 1593), a drawing which gave better

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* The situations of the experimental points are indicated sufficiently here by the approximate values in the columns headed p. e_1 is the mean apparent error of the points, e_2 is the error due to the existence of apparent errors of improbable magnitude, e_3 that due to runs of errors with the same sign ; E, the total error, $= e_1 \times e_2 \times e_3$, and the relative error is the ratio of the total error to the experimental error, e. The relative error, of course, in an acceptable drawing should be nearly unity, as also should the e_2 and e_3 errors, while e_1 and E should be nearly equal to the experimental error. For further details see Phil. Mag. xxxiii. p. 437.

Densities of Soda Solutions.
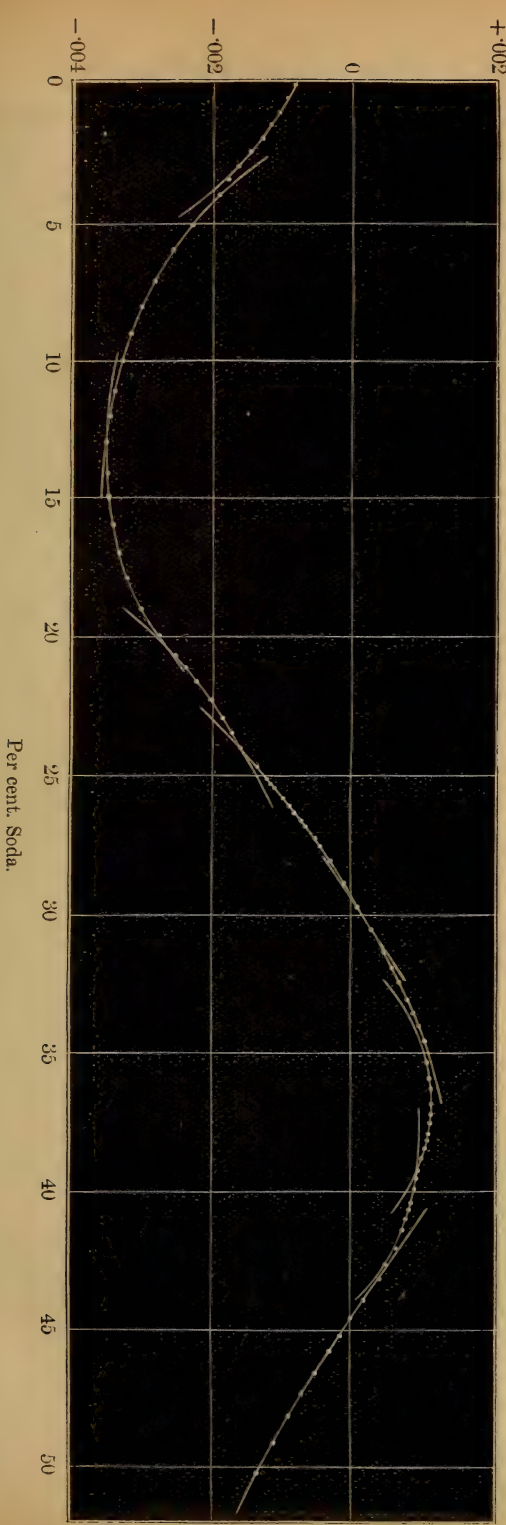
equality here increased, instead of diminished, the total error by giving higher values for the e_2 and e_3 errors.

In columns C and D are given the results of making drawings which obliterate every alternate one of the true breaks. The errors of such drawings, as will be seen, are far in excess of what they should be, being nearly 19 and 33 times greater respectively than the experimental error, and this, too, in spite of the fact that many of the curves for the various sections were much more complicated than those used in the A drawing, the lath having had to be pulled or twisted considerably so as to get even an approximate agreement. This remark applies also, though to a less extent, to the B drawing.

In three cases the sections composing the A figure are drawn so as not quite to meet, namely at 42, 35, and 4 per cent. The densities must, of course, be a continuous function of the strength, and in every perfect drawing the sections, therefore, must meet; but apparent discontinuity might be produced if there were two breaks very close together, with an insufficient number of points to show the existence of both. There is strong evidence from an independent source, as will be mentioned below, to show that two such breaks do actually exist in the neighbourhood of 42 per cent., and in the face of such evidence it has been considered safer not to strain the drawing so as to make the sections meet in cases where the lie of the adjacent points seems strongly to favour their not doing so.

In the case of the break at about 4 per cent., the first section certainly seems inapplicable beyond 3 per cent., while the second section, extending to 12 per cent., does not seem to apply back beyond 4 per cent.; and in this case the intermediate experimental point at 3·5 per cent. would lie on a short connecting curve, for the drawing of which there are not sufficient data; it has, therefore, been omitted entirely in the examination of the drawing (column A, Table II.).

It remains to be seen whether the breaks in the densities, which thus seem to be so well established, correspond or not with the composition of the hydrates of soda which have been isolated in the crystalline condition. The examination of the freezing-points of soda solutions (Chem. Soc. Trans. 1893, p. 890) showed that from solutions up to 20 per cent. strength water crystallized, after which various definite hydrates to the number of eight or nine separated, till a strength corresponding to $NaOH\,H_2O$ was reached, beyond which the investigations were not extended.

Breaks in Densities.		Hydrates isolated, and Breaks in freezing-point figure.		
42·6 p. c. NaOH	....	{ 41·67 p. c. NaOH { (42·55	=NaOH, $3\frac{1}{9}$ H$_2$O isolated. „ =NaOH, 3H$_2$O)	
38·77 „	....	38·83 „	=NaOH, 3·5H$_2$O	„
35·0 „	....	35·71 „	=NaOH, 4H$_2$O	„
29·4 „	....	30·77 „	=NaOH, 5H$_2$O*	„
24·05 „	....	24·10 „	=NaOH, 7H$_2$O	„
20·0 „	....	19·80 „	=NaOH, 9H$_2$O	„ ?
12·1 „	....	12·3 „	=NaOH, 16H$_2$O break.	
3–4 „	....	4 „	=NaOH, 53H$_2$O	„

The above list gives the positions of the eight breaks established by the densities, and of these, it will be seen, six certainly agree with six of the hydrates which have been isolated in the crystalline condition; and, although the remaining two occur in the region of weak solutions where no hydrates were actually isolated, still the freezing-points in this region show two well-marked breaks (and these were the only two shown here), and both of these agree well with those in the density-figure.

Such a thorough agreement between the breaks and the hydrates isolated must, I think, settle definitely that these breaks are really due to the hydrates present in solution.

The first isolated hydrate mentioned in the above list is a complex one, NaOH,$3\frac{1}{9}$H$_2$O, or, as I pointed out at the time (*loc. cit.* p. 894), probably a molecular compound of 8(NaOH,3H$_2$O) with NaOH,4H$_2$O. But the existence of such a complex necessitates also the existence of the hydrate NaOH, 3H$_2$O, though it itself was not actually isolated, and it is this tri-hydrate, and not the complex of it with the tetrahydrate, which seems to be shown by the densities. The composition of the trihydrate and its complex differs but little, and the density-determinations could not possibly have shown a break corresponding to each. It is probably due to the existence of the undiscovered break here that the densities appear to be slightly discontinuous.

A similar explanation may hold good in the case of the apparent discontinuity at the tetrahydrate : two hydrates of about this composition were, as a matter of fact, isolated, and, although the analytical numbers pointed to their being

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* The composition of this hydrate, as given by experiment, was NaOH, $5\frac{2}{11}$H$_2$O, containing 30·01 per cent. soda. This value agrees better with the position of the density-break than does the pentahydrate entered in the table. The freezing-points, however, were scarcely sufficient to settle whether it was a pentahydrate or the more complex hydrate mentioned.

actually isomeric, yet they may not really be so, for the composition of such hydrates cannot be determined very exactly. It may be remarked that the break at the tetrahydrate can be more easily bridged over than any of the others : that at 12 per cent. is also a comparatively feebly marked break.

There was some doubt as to whether the nonohydrate was really isolated or not : the crystallization of it, if it occurred, took place just at a point where the freezing-point figure undergoes a great general change, where the crystallization of water ceases and that of the hydrates begins, and it is interesting to notice that this is just the point at which the irregularities of the density-figure begin to be very prominent. The values for the densities *minus* $(1 + \cdot 0105\, p)$ show this fact rather more clearly than those plotted in the diagram.

It might be expected that at the point where a break occurs, and where there must be present a larger amount of the hydrate of the composition indicated by the break than there is in a solution of any other strength, the volumes of the solutions would show a comparative minimum, and the densities a comparative maximum.   But this is not necessarily the case, unless the formation of the hydrate is always accompanied by contraction, and the present results show that contraction does not always occur : indeed, most of the breaks seem to occur at points where the densities are at comparative minima (in the diagram a relative increase in the densities will be shown by the figure rising towards the top of the page).

I have examined the first differences of the densities and give the values for them in Table III., but they do not form a figure nearly so suitable for examination as those already mentioned.   This is in part due to the smallness of the differences between many of the consecutive determinations.   All that can be said of the nature of the differential figure is that it is rectilineal within the limits of experimental error between any two breaks.   In this it resembles the results with potash, calcium chloride, and calcium nitrate, and confirms Mendeléeff's statement as to the general nature of densities ; though it must be remembered that in the two cases on which this statement was chiefly founded—sulphuric acid and alcohol—the first differences are conspicuously rectilineal (see Mendeléeff, " Solutions," and Chem. Soc. Trans. 1887, p. 779 ; Pickering, Chem. Soc. Trans. 1890, p. 79, and *Zeit. f. physikal. Chem.* vi. p. 10).   The theoretical considerations which led Mendeléeff to conclude that the first differences must be absolutely rectilineal are, no doubt, mistaken ; they

depended on the supposition that never more than two hydrates coexisted in solution, whereas my results with the freezing-points of soda solutions prove that at least four or five hydrates may coexist (Chem. Soc. Trans. 1893, p. 897).

Table IV. gives the densities of soda solutions for every round value of percentage strength, as constructed from the readings of a figure similar to that in the diagram, the values having been differentiated and the differences plotted out in order to detect any errors which may have been made in taking the readings.

Results with Potash.

The results with potash (Table V.) are much less interesting than those with soda. They have been plotted out in a variety of ways, and indicate the probable existence of four breaks; but none of these are by any means well marked, and they would not repay the trouble of a more critical examination. The probable positions of these breaks are :—

43·2 per cent. corresponding to $KOH + 4·05 \ H_2O$.
35·4   ,,   ,,   ,, $KOH + 5·68 \ H_2O$.
19·0   ,,   ,,   ,, $KOH + 13 \ \ \ H_2O$.
8·0   ,,   ,,   ,, $KOH + 36 \ \ \ H_2O$.

The first of these agrees with the recently isolated tetra-hydrate (Chem. Soc. Trans. 1893, p. 298), and the second occurs at the point where water ceases to crystallize from the solution and the tetrahydrate begins to do so—a so-called cryohydric point in fact. In many cases it has been found that such a change of crystallization occurs at a point corresponding to the composition of a hydrate existing, according to independent evidence, in solution.

It is noticeable that the densities in the case of potash increase at an increasing rate with the strength, the reverse being the case with soda. The sixth column in Table V. gives the volume of unit weight of the potash in solution calculated on the assumption that the water present occupies the same volume as it would do if it were free.

Table VI. contains the values for round percentage numbers.

TABLE I.—Densities of Sodium-Hydroxide Solutions at 15° C.

p=per cent. NaOH,　s=density,　$a=1+\cdot011639p-\cdot000020143p^2$, v=volume of unit weight of solution.

The values marked by asterisks are the means of the preceding bracketed observations.

p.	s.	$s-(1+\cdot0105p)$.	$s-a$.	v.
50·1960	1·532153	·005095	− ·001326	·652676
⎰ 49·2074	1·522853	·006175	− ·001108 ⎱	
⎱ 49·1799	1·522542	·006153	− ·001144 ⎰	
*49·1937	1·522698	·006164	− ·001126	·656729
48·1799	1·513121	·007232	− ·000889	·660886
⎰ 47·2875	1·504642	·008123	− ·000696 ⎱	
⎱ 47·2845	1·504655	·008167	− ·000653 ⎰	
*47·2860	1·504649	·008146	− ·000675	·664607
⎰ 46·3058	1·495307	·009096	− ·000455 ⎱	
⎱ 46·2782	1·495074	·009153	− ·000418 ⎰	
*46·2920	1·495191	·009125	− ·000437	·668811
45·6402	1·488979	·009757	− ·000269	·671601
45·1580	1·484368	·010209	− ·000150	·673687
44·5399	1·478446	·010777	·000006	·676386
43·7205	1·470565	·011500	·000205	·680011
42·8516	1·462191	·012249	·000430	·683906
42·3473	1·457289	·012642	·000531	·686206
⎰ 41·8570	1·452532	·013033	·000649 ⎱	
⎱ 41·8341	1·452332	·013074	·000677 ⎰	
*41·8456	1·452432	·013053	·000663	·688501
41·4823	1·448880	·013316	·000729	·690188
⎰ 41·0084	1·444227	·013639	·000804 ⎱	
⎱ 40·9571	1·443719	·013669	·000808 ⎰	
*40·9828	1·443973	·013654	·000806	·692534
40·6385	1·440603	·013899	·000877	·694154
40·2803	1·437068	·014125	·000928	·695861
⎰ 40·0388	1·434665	·014258	·000954 ⎱	
⎱ 39·9525	1·433833	·014332	·000978 ⎰	
*39·9907	1·434249	·014347	·000966	·697229
39·4735	1·429086	·014614	·001040	·699748
⎧ 39·1299	1·425650	·014786	·001059 ⎫	
⎨ 39·0948	1·425263	·014768	·001025 ⎬	
⎩ 39·0893	1·425273	·014840	·001095 ⎭	
*39·1012	1·425395	·014832	·001060	·701560
⎧ 38·7538	1·421879	·014964	·001076 ⎫	
⎨ 38·7087	1·421467	·015026	·001118 ⎬	
⎩ 38·6917	1·421256	·014993	·001079 ⎭	
*38·7181	1·421534	·014994	·001091	·703465
38·3114	1·417469	·015199	·001128	·705483
38·0139	1·414505	·015349	·001169	·706961
37·8413	1·412766	·015432	·001174	·707831
⎰ 37·5551	1·409844	·015515	·001149 ⎱	
⎱ 37·4696	1·409050	·015619	·001222 ⎰	
*37·5124	1·409447	·015567	·001186	·709498
37·1163	1·405462	·015741	·001214	·711510

Table I. (*continued*).

$p.$	$s.$	$s-(1+\cdot0105p).$	$s-a.$	$v.$
36·7254	1·401499	·015886	·001224	·713522
36·2208	1·396354	·016036	·001206	·716151
35·8588	1·392648	·016131	·001188	·718056
35·2636	1·386524	·016256	·001140	·721228
34·7427	1·381178	·016380	·001122 ⎫	
34·6623	1·380350	·016396	·001116 ⎬	
34·6489	1·380228	·016414	·001132 ⎭	
*34·6845	1·380585	·016398	·001123	·724331
34·0746	1·374227	·016444	·001020	·727682
33·3818	1·367003	·016494	·000918	·731527
33·0444	1·363487	·016521	·000878 ⎱	
32·7805	1·360653	·016458	·000786 ⎰	
*32·9125	1·362070	·016490	·000832	·734177
32·3022	1·355645	·016472	·000697 ⎱	
32·2260	1·354870	·016497	·000711 ⎰	
*32·2641	1·355258	·016485	·000704	·737867
31·5845	1·348052	·016410	·000534 ⎱	
31·5723	1·347975	·016466	·000599 ⎰	
*31·5784	1·348014	·016441	·000567	·741832
31·0552	1·342460	·016380	·000435 ⎱	
31·0041	1·341900	·016357	·000406 ⎰	
*31·0297	1·342180	·016368	·000421	·745056
30·3376	1·334827	·016282	·000268	·749161
29·6801	1·327797	·016156	·000094	·753127
28·9821	1·320336	·016024	— ·000067 ⎱	
28·8140	1·318458	·015911	— ·000184 ⎰	
*28·8981	1·319397	·015967	— ·000126	·757922
28·1895	1·311761	·015771	— ·000330	·762334
27·5922	1·305298	·015580	— ·000513	·766109
27·3651	1·302849	·015515	— ·000569 ⎱	
27·3639	1·302816	·015495	— ·000590 ⎰	
*27·3645	1·302833	·015506	— ·000580	·767558
27·0107	1·298969	·015357	— ·000713	·769841
26·8222	1·296970	·015337 ⎱	— ·000722 ⎱	
26·6834	1·296834	·015278 ⎰	— ·000781 ⎰	
*26·8186	1·296902	·015307	— ·000752	·771068
26·6645	1·295224	·015247	— ·000803	·772067
26·2480	1·290716	·015112	— ·000907	·774764
25·8480	1·286357	·014953	— ·001030	·777389
25·5536	1·283106	·014793	— ·001159	·779359
25·3713	1·281116	·014718	— ·001214	·780570
25·0994	1·278158	·014614	— ·001284	·782376
24·7197	1·273998	·014441	— ·001405	·784931
24·2481	1·268787	·014182	— ·001594 ⎫	
24·1745	1·267962	·014130	— ·001633 ⎬	
24·1572	1·267849	·014198	— ·001562 ⎭	
*24·1933	1·268199	·014169	— ·001596	·788520
23·6467	1·262229	·013939	— ·001732	·792249
23·1700	1·257017	·013732	— ·001845	·795534
22·5921	1·250618	·013401	— ·002051 ⎱	
22·5538	1·250281	·013466	— ·001976 ⎬	
22·4753	1·249332	·013341	— ·002083 ⎰	
*22·5404	1·250077	·013403	— ·002037	·799951

Table I. (*continued*).

p.	s.	s−(1+·0105p).	s − a.	v.
⎰ 21·8937	1·242939	·013055	− ·002227 ⎱	
⎱ 21·7603	1·241466	·012983	− ·002264 ⎰	
*21·8270	1·242203	·013019	− ·002246	·805021
21·0501	1·233609	·012583	− ·002467	·810629
20·5676	1·228269	·012309	− ·002596	·814154
20·0238	1·222178	·011926	− ·002782	·818211
19·1496	1·212525	·011454	− ·002970	·824725
17·9519	1·199230	·010735	− ·003221	·833869
⎰ 17·0603	1·189404	·010271	− ·003299 ⎱	
⎱ 17·0034	1·188731	·010195	− ·003348 ⎰	
*17·0319	1·189068	·010233	− ·003324	·840995
⎰ 16·0479	1·178141	·009638	− ·003453 ⎱	
⎱ 16·0238	1·177909	·009657	− ·003420 ⎰	
*16·0359	1·178025	·009648	− ·003437	·848878
⎰ 15·1867	1·168576	·009116	− ·003537 ⎱	
⎱ 14·9431	1·165909	·009007	− ·003515 ⎰	
*15·0649	1·167243	·009061	− ·003526	·856720
⎰ 14·0643	1·156152	·008477	− ·003558 ⎱	
⎱ 14·0451	1·155971	·008497	− ·003526 ⎰	
*14·0547	1·156062	·008488	− ·003542	·865006
13·0003	1·144364	·007861	− ·003543	·873848
12·1267	1·134670	·007340	− ·003511	·881313
11·1000	1·123272	·006722	− ·003439	·890256
10·0435	1·111551	·006094	− ·003313	·899644
9·0576	1·100617	·005512	− ·003152	·908581
8·1040	1·090020	·004928	− ·002979	·917414
7·0833	1·078655	·004280	− ·002777	·927080
6·0376	1·067015	·003620	− ·002523	·937194
5·0728	1·056280	·003016	− ·002243	·946718
⎰ 4·0816	1·045233	·002376	− ·001939 ⎱	
⎱ 4·0513	1·044894	·002355	− ·001928 ⎰	
*4·0665	1·045064	·002366	− ·001934	·956879
⎰ 3·6052	1·039886	·002031	− ·001813 ⎱	
⎱ 3·5457	1·039213	·001983	− ·001802 ⎰	
*3·5755	1·039650	·002007	− ·001808	·961955
⎰ 3·0253	1·033393	·001627	− ·001634 ⎱	
⎱ 3·0139	1·033272	·001626	− ·001624 ⎰	
*3·0196	1·033333	·001627	− ·001629	·967742
⎰ 2·6359	1·029019	·001342	− ·001521 ⎱	
⎱ 2·5139	1·027712	·001316	− ·001420 ⎰	
*2·5749	1·028366	·001330	− ·001471	·972416
1·9907	1·021821	·000919	− ·001269	·978645
1·5752	1·017110	·000570	− ·001174	·983178
1·0209	1·010816	·000097	− ·001018	·989300
0·5271	1·005220	− ·000315	− ·000909	·994807
0	·999180	− ·000820	− ·000820	1·000821

TABLE II.—Examination of the Densities of Sodium-Hydroxide Solutions by the Graphic Method.

Apparent errors of the experimental points expressed in terms of the density $\times 10^6$. Mean experimental error $= 6\cdot31$.

A. Apparent errors according to a drawing showing breaks at 3 to 4, 12·1, 20·0, 24·05, 29·40, 35·0, 38·77, and 42·6 per cent.
B. Apparent errors according to a drawing showing breaks at 1·8, 7·8, 16, 22, 26·7, 32·2, 36·9, 40·7, and 46·4 per cent.
C. Apparent errors according to a drawing showing breaks at 12·1, 24·05, 35, and 42·6 per cent.
D. Apparent errors according to a drawing showing breaks at 3·5, 20·0, 29·4, and 38·77 per cent.

p.	A.	B.	C.	D.
50·2	+20	......	+20	+37·5
49·2	− 7·5	......	− 7·5	+ 5
48·2	− 2·5	......	− 2·5	+10
47·3	0	......	0	+ 5
46·3	0	0	0	− 2·5
45·6	0	0	0	− 10
45·2	+ 2·5	+ 2·5	+ 2·5	−12·5
44·5	0	− 7·5	0	−27·5
43·7	0	− 5	0	−25
42·9	+ 2·5	+12·5	+ 2·5	− 5
42·3	0	+ 2·5	0	−15
41·8	+ 2·5	+12·5	+ 5	0
41·5	+ 5	+17·5	+10	+ 7·5
41·0	−22·5	−12·5	−15	−15
40·6	0	0	+ 5	+ 5
40·3	− 5	+ 5	− 2·5	+ 2·5
40·0	− 5	+ 7·5	− 5	+ 5
39·5	+17·5	+27·5	+ 5	+20
39·1	+ 5	+ 5	−20	+10
38·7	− 2·5	−12·5	−27·5	−15
38·3	− 5	− 5	−20	−12·5
38·0	+ 2·5	+ 7·5	− 5	− 5
37·8	− 5	0	+10	−12·5
37·5	−10	− 7·5	− 7·5	−17·5
37·1	+ 5	+ 5	+17·5	+ 5
36·7	+12·5	+ 5	+20	+ 7·5
36·2	0	− 2·5	+ 5	0
35·9	0	− 5	+ 2·5	− 2·5
35·3	− 7·5	−12·5	− 1·25	−10
34·7	+25	+30	+25	+32·5
34·1	− 5	0	− 7·5	+ 2·5
33·4	+ 2·5	+ 5	− 7·5	+ 2·5
32·9	+10	+12·5	− 5	+ 7·5
32·3	0	0	− 7·5	+ 2·5
31·6	+ 7·5	+ 5	+ 5	+ 1·75
31·0	−15	−20	−15	− 5
30·3	+ 7·5	+ 7·5	+10	+15
29·7	0	+ 2·5	+ 7·5	+10
28·9	0	− 5	+ 5	+ 5

Table II. (*continued*).

p.	A.	B.	C.	D.
28·2	+ 2·5	− 2·5	0	+ 5
27·6	+ 2·5	0	0	+ 5
27·4	0	− 5	− 2·5	0
27·0	−25	−17·5	−20	−15
26·8	− 5	0	− 2·5	0
26·7	0	+ 2·5	0	0
26·2	+17·5	+ 2·5	+12·5	+15
25·8	+27·5	+45	+25	+22·5
25·6	−10	− 5	−15	−20
25·4	− 7·5	− 5	−15	−20
25·1	+ 7·5	+15	+ 7·5	−25
24·7	+ 7·5	+10	+ 7·5	−10
24·2	−10	−27·5	−10	−47·5
23·6	0	− 7·5	+ 5	−27·5
23·2	+10	+15	+25	+ 2·5
22·5	− 2·5	+ 5	+20	+ 7·5
21·8	− 5	+ 2·5	+20	+ 7·5
21·1	0	+30	+17·5	+ 7·5
20·6	+ 7·5	+30	+ 7·5	+ 5
20·0	−25	−15	−35	−30
19·1	+12·5	+25	−20	+ 7·5
18·0	−20	−32·5	−45	0
17·0	+17·5	+ 2·5	− 7·5	+32·5
16·0	+ 2·5	+ 5	− 5	+22·5
15·1	−15	−10	−20	−10
14·1	+ 7·5	+ 7·5	+ 5	− 5
13·0	+ 2·5	0	− 2·5	−22·5
12·1	+10	− 2·5	− 5	−27·5
11·1	0	− 5	− 7·5	−22·5
10·0	− 5	− 7·5	−12·5	− 2·5
9·1	+12·5	+ 5	0	+27·5
8·1	+ 2·5	− 5	− 7·5	+15
7·1	− 5	+ 5	−10	0
6·0	−10	− 2·5	− 5	−12·5
5·1	+ 5	+ 2·5	+ 2·5	− 7·5
4·1	0	+ 7·5	0	− 5
3·6	......	−17·5	−22·5	......
3·0	− 2·5	−15	−20	− 2·5
2·6	0	+10	+ 7·5	0
2·0	+ 7·5	+27·5	+27·5	+ 7·5
1·6	−12·5	......	+22·5	−12·5
1·0	0	......	+22·5	0
0·5	0	......	+15	0
0	0	......	0	0
Sum ...... $\left\{\begin{array}{l}\\\\\end{array}\right.$	+290 −230	+427·5 −277·5	+407 −460	+405 −495
e_1	6·27	9·40	10·46	10·98
e_2	1·61	4·14	4·80	5·44
e_3	1	1·19	2·33	3·44
E	10·1	41·3	116·99	205·52
Rel. Error ...	1·60	6 55	18·54	32·57

TABLE III.—First Differences of the Densities of Sodium-Hydroxide Solutions at 15°.

ds/dp.	p.	ds/dp.	p.	ds/dp.	p.
·009433	49·69	·010255	34·97	·011062	21·44
·009447	48·69	·010424	34·38	·011067	20·81
·009478	47·73	·010427	33·73	·011201	20·30
·009515	46·79	·010511	33·15	·011042	19·59
·009530	45·97	·010506	32·59	·011101	18·55
·009562	45·40	·010564	31·92	·011046	17·49
·009581	44·85	·010632	31·30	·011087	16·53
·009618	44·13	·010624	30·68	·011104	15·55
·009638	43·29	·010692	30·01	·011068	14·56
·009720	42·60	·010742	29·29	·011095	13·53
·009681	42·10	·010776	28·54	·011097	12·56
·009777	41·66	·010821	27·89	·011102	11·61
·009824	41·23	·010826	27·48	·011094	10·57
·009788	40·81	·010921	27·19	·011090	9·55
·009869	40·46	·010760	26·91	·011112	8·58
·009734	40·14	·010889	26·74	·011135	7·59
·009983	39·73	·010824	26·46	·011131	6·56
·009914	39·29	·010898	26·05	·011127	5·56
·010078	38·91	·011043	25·70	·011146	4·57
·009995	38·51	·010916	25·46	·011026	3·81
·009963	38·16	·010879	25·24	·011364	3·30
·010075	37·93	·010956	24·91	·011169	2·80
·010091	37·68	·011016	24·46	·011203	2·28
·010060	37·31	·011922	23·92	·011338	1·78
·010128	36·92	·010933	23·41	·011355	1·30
·010204	36·47	·011023	22·86	·011332	0·77
·010237	36·04	·011037	22·18	·011459	0·26
·010289	35·56				

TABLE IV.—Densities of Sodium-Hydroxide Solutions at 15°.

P. cent. NaOH.	Density.	P. cent. NaOH.	Density.	P. cent. NaOH.	Density.
0	0·999180	17	1·188707	34	1·373453
1	1·010611	18	1·199783	35	1·383815
2	1·021920	19	1·210861	36	1·394092
3	1·033109	20	1·221933	37	1·404279
4	1·044317	21	1·233062	38	1·414363
5	1·055463	22	1·244119	39	1·424353
6	1·066602	23	1·255134	40	1·434299
7	1·077733	24	1·266092	41	1·444161
8	1·088856	25	1·277063	42	1·453929
9	1·099969	26	1·287990	43	1·463623
10	1·111069	27	1·298877	44	1·473249
11	1·122165	28	1·309708	45	1·482850
12	1·133250	29	1·320496	46	1·492406
13	1·144353	30	1·331213	47	1·501927
14	1·155450	31	1·341879	48	1·511412
15	1·166538	32	1·352472	49	1·520868
16	1·177619	33	1·362991	50	1·530282

TABLE V.—Densities of Solutions of Potassium Hydroxide at 15°.

Molecular Volume of one gram of Hydroxide

$$= \frac{\dfrac{1}{s} - (100-p)\cdot 99918}{p}.$$

Per cent. KOH (p).	Sp. gr., Water at 15°=1.	Density (s), Water at 4°=1.	$(s-1) - \dfrac{p}{100}$.	Vol. of 1 gram. solution.	Volume of hydroxide.	ds/dp.	p.
51·4170	1·532506	1·531250	+·017080	·531250	·324469	·011954	50·96
,,	1·532475	1·531211	+·017041	·653078	·324506	·011917	50·00
50·5035	1·521558	1·520310	+·015275	·657760	·321537	·011788	49·04
49·4987	1·509573	1 508336	+·013349	·662984	·318301	·011804	48·16
48·5876	1·498825	1·497596	+·011720	·667737	·315288	·011622	47·29
47·7228	1·488609	1·487388	+·010160	·672319	·312467	·011645	46·37
46·8477	1·478430	1·477218	+·008741	·676948	·309490	·011539	45·43
45·9243	1·467703	1·466499	+·007256	·681896	·306370	·011484	44·53
45·8744	1·467072	1·465868	+·007124	·682189	·306247	·011412	43·66
44·9641	1·456586	1·455392	+·005751	·687100	·303106	·011406	42·86
44·0859	1·446491	1·445305	+·004446	·691895	·300084	·011342	42·06
43·2403	1·436825	1·435647	+·003244	·696550	·297146	·011201	41·31
42·4866	1·428221	1·427050	+·002184	·700746	·294540	·011243	40·53
41·6367	1·418609	1·417410	+·001043	·705510	·291565	·011116	39·67
40·9866	1·411285	1·410128	+·000262	·709157	·298209	·011160	38·86
40·0774	1·401056	1·399906	−·000868	·714334	·285989	·010990	38·05
39·2581	1·391941	1·390799	−·001782	·719011	·282984	·011032	37·22
38·4660	1·383093	1·381959	−·002701	·723611	·280175	·010931	36·42
37·6370	1·373975	1·372848	−·003522	·728412	·277040	·010937	35·60
36·7947	1·364675	1·363556	−·004391	·733377	·273966	·010809	34·77
36·0522	1·356553	1·355440	−·005081	·737768	·271176	·010775	33·84
35·1445	1·346618	1·345513	−·005932	·743211	·267817	·010755	32·65
34·4019	1·338584	1·337486	−·006533	·747671	·264962	·010584	30·95
33·2745	1·326436	1·325349	−·007405	·754512	·260605	·010461	29·03
32·0207	1·312941	1·311864	−·008343	·762274	·255844	·010336	27·17
29·8776	1·290240	1·289182	−·009294	·775685	·247289	·010224	25·33
28·1861	1·272532	1·271487	−·010374	·786481	·240374	·010092	23·32
26·1460	1·251426	1·250400	−·011060	·799744	·231767	·009935	21·19
24·5136	1·234723	1·233710	−·011426	·810563	·224688	·009892	19·24
22·1249	1·210596	1·209604	−·011645	·826717	·213913	·009753	17·19
20·2729	1·192183	1·191205	−·011524	·839486	·205007	·009692	15·20
18·2119	1·171777	1·170817	−·011304	·854104	·195208	·009563	13·13
16·1753	1·151899	1·150954	−·010799	·868844	·184899	·009477	11·09
14·2291	1·133020	1·132091	−·010200	·883321	·175050	·009417	9·09
12·0227	1·111904	1·110992	−·009235	·900097	·163043	·009292	6·99
10·1657	1·094292	1·093394	−·008263	·914583	·152503	·009252	5·00
8·0220	1·074086	1·073206	−·007014	·931809	·140539	·009203	3·39
5·9494	1·054815	1·053949	−·005545	·948813	·126655	·009176	1·36
4·0595	1·037315	1·036464	−·004131	·964818	·113954		
2·7141	1·024924	1·024083	−·003058	·976483	·104122		
0	1·000000	0·999180	−·000820	1·000821	0		

TABLE VI.—Densities of Solutions of Potassium Hydroxide at 15°.

Per cent. KOH.	Density.	Per cent. KOH.	Density.	Per cent. KOH.	Density.
52	1·53822	34	1·33313	16	1·14925
51	1·52622	33	1·32236	15	1·13955
50	1·51430	32	1·31166	14	1·12991
49	1·50245	31	1·30102	13	1·12031
48	1·49067	30	1·29046	12	1·11076
47	1·47896	29	1·27997	11	1·10127
46	1·46733	28	1·26954	10	1·09183
45	1·45577	27	1·25918	9	1·08240
44	1·44429	26	1·24888	8	1·07302
43	1·43289	25	1·23866	7	1·06371
42	1·42150	24	1·22849	6	1·05443
41	1·41025	23	1·21838	5	1·04517
40	1·39906	22	1·20834	4	1·03593
39	1·38793	21	1·19837	3	1·02671
38	1·37686	20	1·18839	2	1·01752
37	1·36586	19	1·17855	1	1·00834
36	1·35485	18	1·16875	0	0·99918
35	1·34396	17	1·15898		

XXXIII. "*Densities in the Earth's Crust.*"
By Rev. O. Fisher, *M.A., F.G.S.*[*]

IN a letter which appears under the above heading in the February number of this Magazine, Mr. Jukes-Browne expresses a wish that I would either admit or deny the value of Professor Blake's criticism [†] upon my conclusions concerning the comparative densities and thicknesses of the layers of the earth's crust beneath the oceans and continents respectively.

I do not feel much doubt about the correctness of my work upon this subject, because it was under very careful consideration for several weeks, not only by myself but also by Mr. Brill, whose mathematical ability is unquestionable ; and I think Mr. Blake has thrown it aside as unworthy of his consideration rather too hastily. If he had more fully mastered my results, he would not have stated in his first paragraph that " the argument about the underlying layers of the crust seems to depend on the greater density of the superficial layer in continental than in oceanic areas "—which is the exact opposite to the conclusion at which I have

[*] Communicated by the Author.
[†] 'Annals of British Geology,' 1892. Introductory review.

arrived !* Mr. Blake does not appear to have realized the argument from cap sectors, because he writes of a cap sector beneath the ocean " and another cap sector beneath the land." This was not the idea which I tried to work out.

The subject will be made more intelligible by means of a diagram. The definition of a cap sector was borrowed from the fifth volume of the 'Account of the Great Trigonometrical Survey of India,' where approximate expressions for the vertical attraction at the apex A of a sector will be found. In my work a cap sector under consideration may be supposed to be partly in the oceanic area and partly in the land ; the object being to determine what different arrangements in regard to density and thickness of the layers in any part of it would have equal effects in contributing to gravity at the point A, it being known from M. Faye's investigations † that, when A is on the ocean, gravity will be the same for all positions of A.
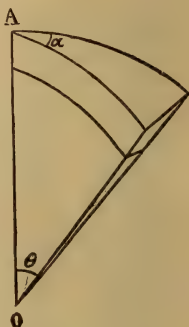
The exact expression for the attraction at A for a complete circular cap is given in Pratt's 'Figure of the Earth,' 4th ed. § 68 ; and to alter it to the case of a sector it is only needful to replace 2π by the sector angle α.

His expression is of course obtained for the Newtonian law of attraction, and it would be absurd for the case of nature to assume any other ‡. Putting α for the sector angle instead of 2π, τ for the density of the sector, t for its thickness, and a for the radius O A, it can obviously be expanded in a series so that

vertical attraction at A

$$= \alpha \left\{ \tau t f(\theta) + \tau \frac{t^2}{a} \phi(\theta) + \tau \frac{t^3}{a^2} \psi(\theta) + \&c. \right\},$$

where $f(\theta)$, $\phi(\theta)$, $\psi(\theta)$, &c. are (not "unknown" but) known functions of θ.

* 'Physics of the Earth's Crust,' 2nd edit., bottom of p. 246. Also Appendix to the same, p. 7.

† *Comptes Rendus*, March 22, 1886.

‡ In fact the ocean could not be in equilibrium unless the spherical shells attracted to their common centre, which could only be in the cases of the laws of the direct distance and of the inverse square.

In fact,
$$f(\theta) = 1 + \sin\frac{\theta}{2},$$

$$\phi(\theta) = -\left(1 + \frac{3}{4}\sin\frac{\theta}{2} + \frac{1}{4\sin\dfrac{\theta}{2}}\right),$$

$$\psi(\theta) = \frac{1}{3} + \frac{1}{8}\sin\frac{\theta}{2} + \frac{5}{24\sin\dfrac{\theta}{2}},$$

&c. = &c.

This answers Mr. Blake's objection that " the definite point where the [supposed] fallacy comes in is the assumption that $f(\theta)$, $\phi(\theta)$, $\psi(\theta)$, &c. are independent." They are not independent, but are all functions of the same variable.

I will now prove my proposition in a slightly different form from that given in my book, out of regard to Mr. Blake's remark that the method is independent of the law of gravitation.

If we are at liberty to assume any other law than the Newtonian, it will be necessary to introduce a factor C to make the dimensions right. Then the vertical attraction of a cap sector, of density τ and thickness t, may with this addition be expressed in the above form. Let this be overlapped by another cap sector, of thickness t_2 and density τ_2, or by any number m of cap sectors. Then the vertical attraction of the composite cap sector at A will be

$$\mathrm{C}\left\{\Sigma_m(\tau t)f(\theta) + \Sigma_m\left(\tau\frac{t^2}{a}\right)\phi(\theta) + \Sigma_m\left(\tau\frac{t^3}{a^2}\right)\psi(\theta) + \&c.\right\}.$$

Now suppose this composite cap sector to be replaced by another of the same areal dimensions with n layers of thicknesses t' &c. and densities τ' &c. The vertical attraction of this other cap sector at A would be

$$\mathrm{C}\alpha\left\{\Sigma_n(\tau't')f(\theta) + \Sigma_n\left(\tau'\frac{t'^2}{a}\right)\phi(\theta) + \Sigma\left(\tau'\frac{t'^3}{a^2}\right)\psi(\theta) + \&c.\right\},$$

and the difference between the vertical attractions which the two sets of layers would produce would be

$$\mathrm{C}\alpha\left\{\left(\Sigma_m(\tau t) - \Sigma_n(\tau't')\right)f(\theta) + \left(\Sigma_m(\tau t^2) - \Sigma_n(\tau't'^2)\right)\frac{\phi(\theta)}{a} + \&c.\right\},$$

If the attractions are the same in the two cases for any length whatever of the sector, *i. e.* for any number of different assumed values of θ, the coefficients of the several functions of the variable must be separately zero.   Therefore

$$\left.\begin{aligned}
\Sigma_m(\tau t) &= \Sigma_n(\tau't') \\
\Sigma_m(\tau t^2) &= \Sigma_n(\tau't'^2) \\
\Sigma_m(\tau t^3) &= \Sigma_n(\tau't'^3) \\
\&c. &= \quad \&c.
\end{aligned}\right\} \quad . \quad . \quad . \quad . \quad (A)$$

Hence what Mr. Blake says appears to be true, that if the vertical attraction at the apex of a cap sector in the case of any assumed law of attraction can be expanded in the above form, the same proposition regarding the thicknesses and densities will hold good.   This will be a remarkable property of the sphere, but it will by no means invalidate any conclusion we can draw from it in the case of the Newtonian law.

Mr. Blake's second objection is that "the same form of equation would result if we had expressed the same supposed arrangement of layers differently, *e. g.* if we had taken them as non-overlapping, or if we had divided one into two, each of half the thickness." This remark shows that my critic has not appreciated the idea correctly.   The quantity a in the expression is the radius to the outside of each layer, and this being the same for them all, they must overlap.

The third objection is, that "it is necessary to assume the equality of the two sides to the same degree of approximation as there are layers in the crust." Not at all!   I have deduced from the equality that two equal and similar areas (or "patches") of any form, of which the layers, whether the same in number or not, and densities are so related, will produce the same gravitational effect at any place, one as the other.   Now since gravity is known to be the same all over the ocean, we must have the gravitational effect of an area of flat land the same as that of an oceanic area of the same size and form, and consequently the layers in these two areas must be related, as shown by the equations (A), no hypothesis as to equality in the numbers of layers being made.   For example, let there be an area of land at P, and a similar one of ocean at Q.   Take a point R in the ocean equidistant from P and Q; then, remembering that the layers are understood to be underlaid by a centrobaric nucleus, the contribution of P

to gravity at R must be equal to that of Q to gravity at R : otherwise gravity at R would not have its normal value. Hence the layers in the area P must be related to those in Q in the manner proved. But it is not by any means necessary that the number m at P should be the same as the number n at Q; and in the particular case which I have shown to be admissible at p. 244, there are at P on the land side two layers, viz. the crust and the substratum, and at Q in the ocean four, namely, the water, two in the crust, and the substratum.

Mr. Blake further objects that the equations may be indeterminate. If they are so, it does not follow that no conclusions can be drawn from them, because some of the unknown quantities may lie within known limits, which will give limiting values for the others ; and this is the method which I have followed. But for the full understanding of the subject reference must be made to chapter xvii. of my book and to chapter xxvi. (Appendix).

Seeing that a further investigation of my equations, suggested by a letter from Mr. Jukes-Browne in ' Nature '*, led me to modify the conclusions given in chap. xvii., I think it will be as well to state the results here, lest any of your readers, not having seen the Appendix, should take the results as stated in chap. xvii. as final :—

" (1) The suboceanic crust dips less deeply into the substratum than does the continental crust at the seaboard.

" (2) The suboceanic crust is less dense in the lower than in the upper portion.

" (3) The lower portion of that crust is also less dense than the substratum beneath it.

" (4) The upper layer of the suboceanic crust is of high density, and quite thin when compared with the whole thickness.

" (5) The substratum beneath the ocean is less dense than beneath the seaboard.

" (6) The continental crust at the seaboard is of uniform density throughout, or, if it does consist of two layers of different density, one of them must be too thin to sensibly affect the gravitational phenomena."

* ' Nature,' vol. xli. p. 54 (1889).

XXXIV. *Experiments on a Fundamental Question in Electro-Optics: Reduction of Relative Retardations to Absolute. By* John Kerr, *LL.D., F.R.S., Free Church Training College, Glasgow*[*].

TO prepare the way, I begin by recalling these well-known facts : that when light passes through an electrostatically strained medium in a direction perpendicular to the line of electric force, it undergoes a uni-axal double refraction, the optic axis coinciding with the line of force : that with reference to this action, dielectrics are divisible into two classes, the positive[†] and the negative[‡], which are optically related to each other in the same way as the positive class of crystals to the negative : that the intensity of the action, or the quantity of optical effect per unit thickness of the dielectric, is measured by the product CF^2, where C is a constant which is characteristic of the medium, and F is the value of the resultant electric force : that the effects are generally observed and examined still, as they were discovered first, by simple experiments with a pair of Nicol's prisms and a slip of strained glass or other phase-difference compensator.

In every such experiment, the effect specified by the compensator is a difference of phases, or a relative retardation ; and we may therefore view it as a resultant effect—that is to say, as the resultant, or the difference, of electrically generated absolute retardations of two component lights whose planes of polarization are parallel and perpendicular to the line of electric force. What, then, are the values of these two absolute retardations in any given case? *What are the two absolute components of any electrically generated relative retardation?* Such is the question here proposed for solution by experiment.

As long ago as 1882, and several years following, I was much occupied at intervals with this interesting question. In the summer of 1885, in some experiments with the dielectric CS_2, I obtained results as decisive as could be desired. Other dielectrics, both solid and liquid, were tried afterwards, but only with partial success, the experimental difficulties being—in some cases—too much for my methods and time. To these cases I shall make no further reference, as I will keep to the one line of experiment, and to those experiments in particular in which the indications were quite

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[*] Communicated by the Author.
[†] Carbon disulphide, the hydrocarbons, &c.
[‡] Amyl oxide, the heavy oils, &c.

regular and unmistakable. With these limitations, the induction extends to four liquid dielectrics, two positive and two negative : and all the experiments point clearly in one direction.

General Result.—It appears that the proper and immediate optical effect of electric strain is a positive or negative retardation of the one component light whose plane of polarization is perpendicular to the line of force, the sign of the retardation being, of course, the same as the nominal sign of the dielectric. Therefore, of two vibrations which are (on Fresnel's hypothesis) perpendicular and parallel respectively to the line of force, it is only the latter that is immediately affected by the electric strain, this *vibration along the line of force* having its velocity of transmission *retarded* or *accelerated* according as the dielectric is of the *positive* class or the *negative*.

I venture to regard this result as a General Law of double refraction in Electro-Optics, though the proof extends only to four different dielectrics. As the best proof that I can offer, I will merely give a condensed historical sketch of the experiments. It will be seen in this way how the law was first suggested and then confirmed by the phases of a new electro-optic effect. It will be seen also that the proof of the law is independent of all hypotheses, independent even of everything previously known in electro-optics.

The Plate Cell is a piece used in all the experiments.
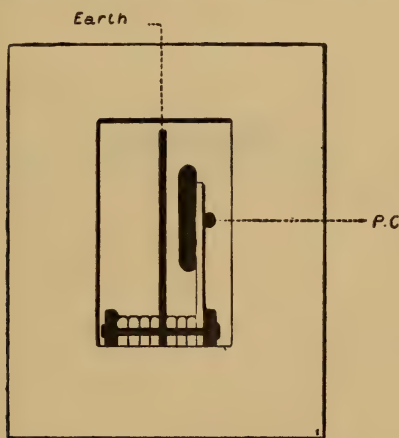
Fig. 1

There is an end-view of it given in the adjacent figure. It consists of five slabs of plate glass, each 10 inches by $7\frac{3}{4}$,

arranged face to face in one block. The inner rectangle represents a tunnel ($5\frac{3}{4}$ by $3\frac{1}{4}$) which passes right through the block. Inside are shown the conductors with supporting frame, the shaded pieces being of brass and the unshaded of plate glass. The lengths of the conductors, at right angles to the plane of the figure (and parallel to the light), are $6\frac{1}{2}$ and $7\frac{1}{2}$ inches, the thickness of the cell being nearly 8 inches. By means of wires which pass through the wall of the cell, the internal conductors are connected with prime conductor and earth, as indicated in the figure. It is understood, of course, that the surfaces of the two conductors are well planed and polished, all corners and edges rounded off, and the two fronting faces accurately parallel. The cell is closed in the usual way, by panes of plate glass laid against the ends; and the whole block is kept together by a screw-press. Two borings in one of the plates provide for the filling and emptying. When the cell is put in order and charged with CS_2, and examined according to the old method, with a pair of crossed nicols, it gives a very pure double refraction, and acts well in all respects, except that (from deficiency of insulation) the largest effect is less than might be expected, hardly amounting to one average wave-length of relative retardation. But this defect is of no great consequence.

The First Experimental Arrangement is shown in the next diagram, in horizontal section through the lamp L and the observer's eye E, but without strict regard to scale.
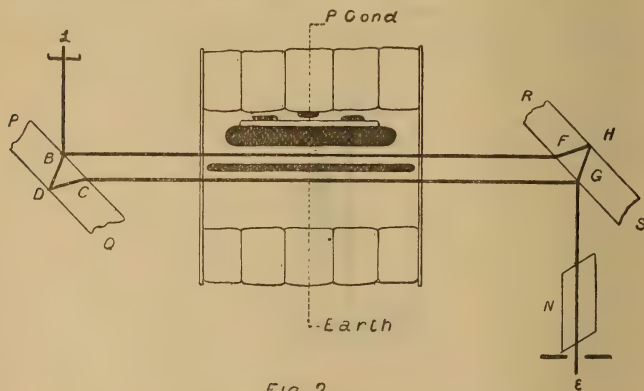
Fig 2.

Two half-inch plates of glass are represented in section by the rectangles PQ, RS. Their function is the same as that of the two plates in Jamin's Interference Refractometer *.

* Preston's Theory of Light, p. 157.

The plates are therefore parallel-surfaced, and of accurately equal thickness, and are silvered on the back as mirrors ; and in their working positions they are almost exactly vertical and parallel, and at 45° to the light. A pencil of light LB, which passes through a vertical slit in front of the lamp, is incident on the first plate at B, and is divided, in the manner shown in the diagram, into two pencils BDCG and BFHG ; and from G the light proceeds anew as one pencil, and passes through a narrow circular diaphragm *, which is fixed at E in front of the observer's eye. The result of the arrangement is, that when the pieces are properly placed, the bright vertical slit L, as seen from E in the direction EG, is crossed by a set of interference-fringes. These are well defined in position by reference to a constant black line, the image of a fine wire which is fixed across the slit L. It may be assumed without argument, that any small increase or decrease of velocity of one of the pencils BF, CG, will produce a positive or negative displacement of the fringes, at the rate of one fringe-width of displacement for every wave-length of relative retardation. As far as the assumption is required, it is easily verified by the introduction of thin plates of glass into the course of the light, anywhere between the two thick plates ; and I find in this way, definitely, that (as the pieces actually stand in the diagram and in all the experiments) an ascent of the fringes indicates a relative retardation of the pencil BF.

There are two essential pieces that remain to be noticed, of which the first is the electro-optic cell. It is shown in the diagram how the laterally separated component pencils pass through the cell, BF through the electric field, and CG through the space electrically screened by the second conductor, this conductor being always to earth. The last piece is a Nicol's prism N, which is placed in the path of either of the single pencils GE, LB, with its principal section laid (1) horizontally and (2) vertically. The design of the apparatus will now be apparent, which is, to give the means of detecting electrically generated changes of velocity of the light BF in two successive cases, when the plane of polarization is (1) perpendicular to the lines of force and (2) parallel to the lines of force. But in actual experiment there is a difficulty encountered at once, which appears at first sight to be insurmountable.

Disturbance of the Fringes.—Suppose all the pieces placed as in the diagram, the cell nearly filled with carbon disulphide, the second internal conductor put permanently to earth, and

* Or otherwise, through a telescope.

the fringes obtained in good form and position. When connexion is made between the first internal conductor and the knob of a charged Leyden jar whose outer coating is to earth, there is an immediate disturbance of the fringes, a set of large and irregular movements, with deformations, ending in the disappearance of the whole system in one or two seconds. The effects are seen better when the first internal conductor is connected permanently with the prime conductor and an attached Leyden jar ; for the potential can then be raised regularly and very slowly from zero, and the full course of the disturbance takes a longer time ; but in other respects the phenomena are the same as before.

When the fringes have been extinguished in this way by the electric action, it is easy to recover them, either by putting the prime conductor to earth, or by keeping the potential at a sensibly constant value high or low for a little time. If with this view the machine be kept working at a constant rate throughout the experiment, the extinguished fringes return gradually into the optical field, and in a little time (20 to 80 turns of the plate) they are as clearly visible as they were before disturbance ; their forms also are good, and their positions approximately constant, though they do not often continue quite motionless in such circumstances even for a fraction of a second. If the prime conductor be now put to earth for a little, and the experiment be then repeated, the disturbance passes through all the same phases as before, though it is more violent at starting as the preceding interval of rest is longer. All these effects come out equally well with common light and with light polarized in the two principal planes.

This optical disturbance is evidently a remote effect of the electric action, produced immediately—not by electric strain —but by irregular changes of density in the medium. We know that in the present cell, as in every like arrangement, the electric action throws the liquid into currents, which pervade all parts of the cell and are very intense at high potential. These material currents explain the changes of density ; for, at starting, they give rise to a rapid process of mixture, forcing denser masses upwards into the course of the light, &c.; and, afterwards, when the mixture is completed, they are still accompanied by irregular variations of pressure in the liquid. It should be easy therefore to imitate the effects by means purely mechanical ; and of this I can give an example from actual observation.

A plate cell, about an inch thick and open at the top, was

charged with water, and placed in the course of the pencils BF, CG, immediately behind the electro-optic cell; and the fringes were obtained in good form and position. The stirring of this water gave a set of optical effects that could not be distinguished from the former disturbance. And when the fringes, extinguished in this way mechanically, were well restored and made moderately steady by regular stirring kept up for a time, I found that a disturbance of the same kind could be obtained at pleasure, either by an interval of rest (the longer the better), or by the addition of a little warm water. But leaving this and returning to the electro-optic experiment, I proceed to show how, in spite of these irregular movements of the fringes, and in the midst of them all, it is possible to obtain a steady effect which corresponds perfectly to the known birefringent action of the medium.

Regular Dislocation of the Fringes.—The electric arrangements are the same as formerly, the two internal conductors being connected permanently, the first with the prime conductor and the second with earth. There is only one change made in the apparatus: the nicol N is withdrawn, and a small rhomb of Iceland spar (about 3 centim. long) is put in its place at E, with principal section horizontal. In this way, the two systems of fringes which were given by the nicol N in succession are now given simultaneously, side by side, and each the exact prolongation of the other: the successive systems (α) of the next diagram are changed into the double system (β, γ).

The machine is now set in motion. The system (β, γ) is disturbed as was the system (α) formerly; but in the midst of the disturbance, and as long as the fringes are clearly
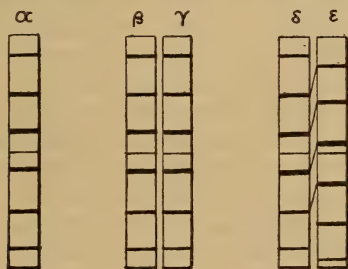
Fig 3.

visible, the sets (β) and (γ) are seen to be relatively displaced, the system (β, γ) being changed into the system (δ, ϵ). The extent of the dislocation increases as the potential rises: that

shown in the diagram, which is about three fourths of the fringe-width, is not much below the highest that can be got with the apparatus. The direction of the dislocation is constant, and indicates a relative retardation of that vibration in the electric field which is parallel to the line of force ; and this agrees with the known character of the medium CS_2 as a positive dielectric.

It is very interesting to watch the two sets of fringes (δ) and (ϵ), and to see them sometimes moving rapidly and very fitfully, but moving always as one system, with its two parts dislocated unchangingly, except so far as the extent of the dislocation varies with varying potential. It is equally interesting to see the effect of spark-discharge of the prime conductor, especially from high potential. At the instant of the spark there is a sudden disappearance of the dislocation, an extremely quick jump of the fringes into line with each other, and this without perceptible check or sudden change of any kind in the disturbance—motion common to the two sets at the time. The best way of observing the effect is to take sparks from prime conductor to earth at stated intervals, while the machine is kept working at some constant rate. The dislocation then reappears immediately after each of the sparks, increasing regularly from zero as the potential rises, and then increasing and decreasing quickly or slowly as the potential rises and falls quickly or slowly. Even when the potential falls most rapidly, as in spark-discharge, the direction of the backward jump is always evident to the eye, otherwise the disappearance of the dislocation in that case is so very quick that one would call it instantaneous.

Very little need be said upon the optical theory of these phenomena. What must be remembered is, that each of the sets of fringes (δ) and (ϵ) is due to the interference of two such pencils as BF and CG reunited in GE, the vibrations being horizontal in one pair of interfering pencils, and vertical in the other pair. With regard to changes of refringent power which are due to mechanical disturbance, it may be assumed that these are independent of the direction of the vibration : both pairs of pencils are therefore similarly and equally affected at each instant, and the corresponding displacements of the two sets of fringes are at each instant similar and equal, however irregularly they may vary from one instant to another. It is otherwise with the birefringent action of the medium ; for here the two pairs of pencils are differently affected at each instant, and the difference is determined solely by value of potential, so that the corresponding effect comes out steadily in the midst of all the irregular changes which are produced by mechanical disturbance of the dielectric.

I think it must be admitted, that in this regular dislocation of the fringes, there is a new and clear presentment of the double refraction which is produced by electric strain. I think also that the new effect is made all the more suggestive by the regularity and perfect steadiness with which it comes out in the midst of the disturbance.

First appearance of the Law.—Before leaving the present experiments I must notice one or two facts observed, but not yet mentioned, that go towards a solution of the question with which we started. The phenomena to which I refer were seen clearly enough in some of the earlier experiments ; but it was only at a later stage that they were well understood, and they were then obtained more regularly.

Beginning with the last form of the experiment, that with the rhomb of Iceland spar as eyepiece. The spar, I should mention, was always so placed that the plane of polarization in the set of fringes (ϵ) was vertical. What I have to notice now is a peculiar feature of the jump of the fringes at the instant of discharge. To a carefully strained, as to an unstrained attention, this jump appeared as a movement of the set of fringes (ϵ) down to the level of the set (δ), never as a movement of the set (δ) up to the level of the set (ϵ). I must say, however, that the accuracy of this perception or judgment was to myself in some degree doubtful, not because of any expectation that could have led to it, but because of the very fugitive character of the phenomenon, and its partial obscuration in many cases by disturbance.

Returning, therefore, to the first form of experiment, that with the nicol N as eyepiece. When the principal section of N was horizontal, and the vibration directed therefore along the line of force, there was a perfectly regular jump of the fringes downwards at the instant of discharge : and at high potential the effect was large and strikingly distinct. When the principal section was vertical, there was nothing regular of this kind seen in any of a large number of observations : there were disturbance-movements at or about the instant of discharge, as before and after, but nothing that could be accepted as a regular jump of the fringes at that instant, always in one direction or always in the other. The interpretation of these results is obvious. I have already stated as a matter of observation, that a rise of the fringes indicates a relative retardation of the pencil BF which passes through the electric field. From the downward jump of the fringes in one of the two cases, we infer therefore that the pencil BF is in that case relatively accelerated in consequence of discharge. But in the present experiment, and with reference to the pencil BF in relation to the pencil CG, it is evident

that relative acceleration and absolute are equivalent ; because it is only in that division of the cell through which the pencil BF passes that there is any sudden physical change at the instant of discharge. It appears therefore, that to relieve the liquid of electric strain is to relieve one of the vibrations (that along the line of force) of an absolute retardation, leaving the perpendicular vibration unaffected.

In several of the later sets of these experiments with CS_2 as dielectric, and with nicol N as eyepiece, I got what appeared to be a perfectly clean liquid. The potential also was made to vary regularly and very slowly; and from both causes the disturbance was very much reduced. The effects then were these :—Principal section of N horizontal : a slow ascent of the fringes during the process of charge, pretty regular, but often obscured and sometimes overpowered by disturbance ; the contrary jump seen always at the instant of discharge. Principal section of N vertical : irregular and generally very small oscillations of the fringes during the process of charge ; but no regular motion in one direction or the other exclusively, either during the process of charge, or at the instant of spark-discharge from high potential.

From all these experiments with CS_2, it seems to follow that of the two principal vibrations, the only one immediately and regularly affected by electric strain is that along the line of force. This conclusion requires and well deserves to be verified ; and I proceed to verify it by another method, or rather by the use of new means.

The Second Experimental Arrangement.—The optical instrument here used is known as Jamin's Interference Refractor for Polarized Light. For a description of it I might refer to a paper already published * ; but I think I ought rather to describe the apparatus here again. The essential pieces are shown in horizontal section in the following diagram.
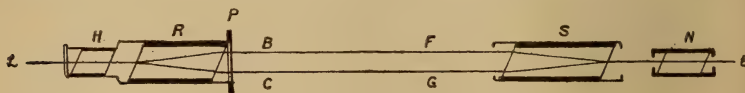
Fig. 4.

R and S are large blocks of Iceland spar, of equal thickness, their principal sections horizontal, and their faces parallel. A pencil of light from a vertical slit L, passes through a Foucault's prism H, and is polarized by it at 45° to the vertical, and then enters the rhomb R. The two pencils emergent from R

* "On the Birefringent Action of Strained Glass." Phil. Mag. for Oct. 1888.

pass immediately through a half-wave plate P, so placed as to interchange the two planes of polarization. Ordinary pencil and extraordinary in the crystal R become thus extraordinary and ordinary in S, and the birefringent action of R is neutralized by that of S. The light enters R and leaves S as a single pencil; but between P and S it passes as a couple of pencils BF and CG, about 14 millim. apart, and polarized in planes vertical and horizontal. The pencil emergent from S is received at E through a Nicol's prism N, which is laid as for extinction with the Foucault H. When all the pieces have been properly placed, the slit L is seen crossed by a set of interference-fringes; and these are modified at pleasure by fine screw-movements of the spar S.

The electro-optic cell is not given in the diagram. It is the same piece as that shown in the diagram of the First Arrangement, and is placed here exactly as there, so that the two laterally separated component pencils pass normally through it, BF through the electric field, and CG behind the second conductor.

The only other optical piece employed in the experiments is a Jamin's glass compensator *, which is placed immediately in front of the spar S: it enables the observer to specify small differences of retardation of the pencils BF and CG.

The results obtained formerly (with nicol N as eyepiece) were fully verified with the new apparatus. The method finally adopted as the best was so similar to the former, and the effects also, that any long description of the experiments would be superfluous. But to give a fair view of the results, I will describe one day's work.

Final Experiments with CS_2.—The first internal conductor connected permanently with prime conductor without Leyden jar, the liquid quite clean, and the conditions of electric work perfect all day. The observations were taken in five successive sets.

First Set.—Plane of polarization of the pencil BF (through the electric field) vertical, or perpendicular to line of force; rise of fringes indicates relative retardation of that pencil. When the fringes were obtained in good form and position, the machine was started, and kept working at a constant rate throughout the experiment. As before, the first effect was a large disturbance, the fringes being displaced and deformed, and disappearing altogether at the second or third turn of the plate; but in a little time (30 or 40 turns) they reappeared in good form and approximately constant position. For distinctness of effect, the central fringe was brought back to

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* Preston's 'Theory of Light,' p. 159.

the line of reference (generally downwards) by a small screw-movement of the spar S ; and then, at every spark from prime conductor to earth, there was a quick downward jump of the fringes, the effect being as distinct as possible from the irregular and slow and generally small movements that went on before and after the spark. As the experiment proceeded, the liquid was more thoroughly mixed, the disturbance decreased, and the effect came out much more purely. Sparks were taken repeatedly at every 3rd, 5th, 10th, 15th turn of the plate ; and the jump was there in every instance, and beautifully distinct. The extent of the jump varied from about $\frac{1}{3}$ of the fringe-width at every 5th turn of the plate, to about $\frac{3}{4}$ at every 10th turn. I should add that the disturbance-movements, though they were greatly reduced at last, were still such as to prevent any good static observation of the fringes.

It is proved clearly by this set of observations, that when the plane of polarization is perpendicular to the line of force, the light is absolutely retarded by electric strain. The spars R and S were now turned round LE through 180°, and the pieces were moved across the optic bench into good position.

Second Set.—Plane of polarization of the pencil BF (through the electric field) horizontal : rise of the fringes indicates a relative retardation of that pencil. The method was the same as in the first set, sparks being taken from prime conductor to earth at regular intervals long and short. When the initial disturbance was over, movements of the fringes were still seen, sometimes in one direction and sometimes in the other, but not exclusively or specially at the instant of discharge. These disturbance-movements were slow and generally small ; and as the experiment proceeded they became very faint, and were occasionally not seen at all for a little time. As to the effect specially looked for, I need only say, that in several scores of observations, taken at different potentials high and low, there was not a trace observed of a regular jump of the fringes at the instant of discharge. It appears, therefore, that when the plane of polarization is parallel to the line of force, the light is neither retarded nor accelerated by electric strain. The spars R and S were now turned back through 180°.

Third Set, the same again as the first. Many observations were taken, and the former effects were obtained regularly ; but they were now more striking, because of the strong contrast with the negative results of the set of observations immediately preceding. The action appeared also to be stronger than before, probably because of improved insulation.

The extent of the jump, taken at every 5th turn of the plate, was now $\frac{1}{2}$ the fringe-width; and at every 10th or 15th turn, it was clearly $\frac{4}{5}$. I find in my notes that this large jump of the fringes impressed me here, again and again, as a thing peculiarly beautiful.

Fourth Set, the same again as the second. The only question in this case was, whether it might still be possible, by the most careful work and under the best conditions attainable, to detect a very small jump of the fringes at the instant of discharge. Many observations were taken at high potential, some at the highest, but without a trace of effect of that kind.

Fifth Set, the same again as the first. The results of first and third sets were recovered regularly. Sparks were then taken, sometimes at every turn of the plate, sometimes oftener. At every spark there was a very small downward jump of the fringes, so small sometimes as to be barely caught, but quite regular and beautifully distinct.

Remarks.—The jump of the fringes was chosen as the principal object of observation, because it was never quite concealed, nor even much obscured, by the mechanical disturbance of the liquid; but I should add that the contrary motion, the gradual ascent of the fringes during the process of charging, was generally evident enough in the experiments, though not often undisturbed or quite regular in its course.

The best observations were got when the fringes happened to continue at rest through a sensible interval of time, including the instant of discharge. The contrast between the two cases was then very remarkable, especially at high potential : in the one case, the beautifully clear jump so often mentioned ; in the other case, no trace of a jump in either direction, generally not even a perceptible shiver of the fringes at the instant of strongest discharge. Instances of this kind occurred not very rarely in the experiments; and there could be no contrast more striking than that between the phenomena in the two cases.

From what I know of the apparatus and its performance, I am sure that no regular and abrupt retardation or acceleration amounting to as much as the *hundredth* part of an average wave-length could have escaped observation in the experiments. It will be remembered also that the jump of the fringes at high potential extended to *four fifths* of the fringe-width. With reference, therefore, to the dielectric CS_2, and the two principal vibrations parallel and perpendicular to the line of force, it appears that the regular effect of the electric strain upon one of the vibrations is a positive retardation, while upon the other vibration there is very probably no effect

whatever, and certainly no effect as large as the *eightieth* part of the former.

Second positive dielectric : a paraffin oil, specific gravity ·845. This liquid was far inferior to CS_2 electrically and also as an optical medium. The method of experiment finally adopted as the best was a little different from that with CS_2. The prime conductor had its capacity enlarged by connexion with a Leyden jar ; the machine was kept working at a constant rate, and the prime conductor was partially discharged, at short and regular intervals, by spark upon the knob of the first internal conductor, which was of course discharged in each interval. The phenomenon looked for was a quick motion of the fringes at the instant of the spark ; that is, at the instant of electric charging of the liquid.

(1) Plane of polarization of the pencil BF (through the electric field) vertical : rise of fringes indicates relative retardation of this pencil. At the instant of the spark there was a quick upward jump of the fringes through something like $\frac{1}{5}$ of the fringe-width, generally followed by a set of large and comparatively slow disturbance-movements. In most cases also, immediately after the spark, the observer was able to detect the contrary jump quite clearly, by laying his finger on the knob of the first conductor. Through a long set of observations taken at different potentials, the upward jump of the fringes at the instant of charging was obtained with perfect regularity ; and—amplitude excepted—the effect was not inferior to that in CS_2.

(2) Plane of polarization of the pencil BF horizontal : rise of fringes indicates relative retardation of BF. Many observations were taken at different potentials, high and low. There were sluggish and irregular disturbance-movements, great and small, but no trace of a regular jump of the fringes in one direction or the other at the instant of the spark. There could be no doubt as to the true meaning of these results. In this positive dielectric, as in CS_2, the vibration along the line of force is retarded by electric strain, and the perpendicular vibration is unaffected.

First negative dielectric : oil of colza. This liquid also was far inferior to CS_2, especially as an optical medium. The method of experiment followed with paraffin was retained here as the best : the first internal conductor was charged by spark from the prime conductor at regular intervals, and was put to earth for a moment in each interval.

(1) Plane of polarization of the pencil BF vertical : rise of fringes indicates relative retardation of BF. The fringes were generally curved and very imperfect at the beginning

of an experiment; but a few successive charges brought them, after some disturbance, into permanently good form, and then there was a quick downward jump seen always at the instant of the spark. And, as in the contrary case of paraffin, this jump was a thing as distinct as possible from the sluggish and irregular disturbance-movements by which it was generally followed. When the spark was taken at every 10th turn of the plate, the potential was about as high as the liquid could bear, and the extent of the jump was fully $\frac{1}{5}$ of the fringe-width. In the course of a long set of observations, this downward jump of the fringes at the instant of charging was seen with perfect regularity, and always distinctly. In this case, therefore, the regular optical effect of electric strain was an acceleration.

(2) Plane of polarization of the pencil BF horizontal: rise of fringes indicates relative retardation of BF. When the fringes were imperfect at starting, the effects of a few successive charges were the same as in the first case, irregular displacements and changes of inclination, the fringes generally rising and falling in their lower and higher parts till they came into permanently good form. Afterwards there were smaller disturbances always present in this case as in the former; but neither there nor here were they such as to interfere ultimately with exact observation. The experiment was carried on for some time till the liquid was well mixed and the fringes good. Many observations were then taken, some of them at highest potential; but there was no trace of a jump ever seen at the instant of the spark. In this liquid, therefore, as in carbon disulphide and paraffin, the only one of the two principal vibrations which is affected by electric strain is that along the line of force; but as the present dielectric is of the negative class, the retardation produced is negative.

Second negative dielectric: seal oil. From want of homogeneity this liquid was very defective optically, the image of the slit L being much deformed and sometimes broken by streaks. The defect was remedied in a good degree by strong charges given to the liquid on both sides of the second conductor. The method of experiment was the same as with oil of colza.

(1) Plane of polarization of the pencil BF vertical: rise of fringes indicates relative retardation of BF. At first, the electricity produced very large displacements and deformations of the fringes, in the midst of which there was no regular effect to be seen; but as the experiment went on, and the medium improved, the expected effect came out distinctly,

a quick downward jump of the fringes at or immediately after the instant of the spark. Under good optical conditions, and at potentials high and low, the effect was perfectly regular, and was as distinct and pure as that in oil of colza, though apparently not quite so large.

(2) Plane of polarization of the pencil BF horizontal: rise of fringes indicates relative retardation of BF. The disturbance of the fringes was greatly reduced as the experiment went on, till at last there was nothing left but a set of slow movements, very irregular and very small, sometimes invisible. In the midst of these as in their absence, and in a long set of observations taken at different potentials from low to highest, there was no trace ever seen of a jump of the fringes at the instant of the spark. It appears, therefore, that in this negative dielectric, as in oil of colza, the total optical effect of electric strain is an acceleration of the vibration which is directed along the line of force.

The conclusion to be drawn from the preceding experiments has been stated already by anticipation ; but I repeat it finally in other terms as follows :—

If light pass through an electrostatically strained medium at right angles to the lines of force, and be represented by two component lights whose planes of polarization are respectively parallel to the lines of force and perpendicular, then the proper and immediate optical effect of the electric strain is a change of velocity of the latter component *.

The use of the words *proper and immediate* in this statement may be thought objectionable ; but some such words are required for the purpose here chiefly intended, which is, to exclude those undoubtedly remote effects of electric action that appeared as disturbances in all the experiments.

Glasgow, February 26, 1894.

XXXV. *On the Behaviour of an Air-Core Transformer when the Frequency is below a certain Critical Value.* By E. C. Rimington†.

[Plates X., XI.]

IT is usually supposed in the case of a transformer whose primary is connected to terminals having an alternating potential difference of constant value between them, that the

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apparent impedance of the primary is diminished on closing the secondary. Under certain conditions, however, this is not the case, as the following investigation will show.

Let r_1 be the resistance of the primary circuit ;

L its inductance ;

r_2 the resistance of the secondary circuit ;

N its inductance ;

M the mutual inductance between the two coils.

The coefficients of induction are assumed constant in the following investigation, a result that can only be obtained in practice when coils not containing iron cores are employed. A pure sine-function alternating P.D. is also assumed.

Let $p = 2\pi n$, where n is the frequency of alternation.

Let e be the value of the P.D. at any instant t, and E its maximum value.

Let c_1 and c_2 be the currents in the primary and secondary circuits respectively, C_1 and C_2 being their maxima.

Let $I_1 = \sqrt{r_1^2 + p^2 L^2}$, the impedance of the primary ;

and $I_2 = \sqrt{r_2^2 + p^2 N^2}$, the impedance of the secondary.

We have the well-known equations,

$$L\frac{dc_1}{dt} + M\frac{dc_2}{dt} + c_1 r_1 = e ; \quad \cdots \quad (1)$$

$$N\frac{dc_2}{dt} + M\frac{dc_1}{dt} + c_2 r_2 = 0. \quad \cdots \quad (2)$$

Differentiate (1) with respect to t, and multiply by N ; differentiate (2) and multiply by M ; then on subtraction we obtain

$$(LN - M^2)\frac{d^2 c_1}{dt^2} + N r_1 \frac{dc_1}{dt} - M r_2 \frac{dc_2}{dt} = N\frac{de}{dt}. \quad (3)$$

Multiply (1) by r_2 and add to (3). This gives

$$(LN - M^2)\frac{d^2 c_1}{dt^2} + (N r_1 + L r_2)\frac{dc_1}{dt} + r_1 r_2 c_1 = r_2 e + N\frac{de}{dt}. \quad (4)$$

Similarly we obtain

$$(LN - M^2)\frac{d^2 c_2}{dt^2} + (N r_1 + L r_2)\frac{dc_2}{dt} + r_1 r_2 c_2 = -M\frac{de}{dt}. \quad (5)$$

Now it is obvious, if the P.D. be a pure sine function and the coefficients constants, that the currents must also be pure sine functions differing only in phase from the P.D.

Assume *, then,

$$c_1 = C_1 \sin pt, \quad c_2 = C_2 \sin (pt + \theta), \quad \text{and} \quad e = E \sin (pt + \phi),$$

$$\frac{dc_1}{dt} = p C_1 \cos pt \quad \text{and} \quad \frac{d^2 c_1}{dt^2} = -p^2 C_1 \sin pt ;$$

also $\dfrac{de}{dt} = p E \cos (pt + \phi).$

Inserting these values in equation (4) gives

$$C_1 \left[\{ r_1 r_2 - p^2 (LN - M^2) \} \sin pt + p (N r_1 + L r_2) \cos pt \right]$$
$$= E r_2 \sin (pt + \phi) + E p N \cos (pt + \phi). \quad . \quad . \quad (6)$$

For shortness, let

a denote $r_1 r_2 - p^2 (LN - M^2)$, and

b denote $p (N r_1 + L r_2).$

Then (6) may be written

$$C_1 \sqrt{a^2 + b^2} \sin (pt + \psi) = E I_2 \sin (pt + \phi + \chi), \quad . \quad (7)$$

where

$$\tan \psi = \frac{b}{a} \quad \text{and} \quad \tan \chi = \frac{p N}{r_2}.$$

As (7) must hold for all values of t, it follows that

$$C_1 \sqrt{a^2 + b^2} = E I_2,$$

or

$$C_1 = \frac{E I_2}{\sqrt{a^2 + b^2}}, \quad , \quad . \quad . \quad . \quad . \quad (8)$$

and that $\psi = \phi + \chi$, or $\phi = \psi - \chi.$

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* This assumption will evidently give a particular solution to equation (4), viz. $c_1 = C_1 \sin pt$.

The complete solution is obtained by adding to this the solution of equation (4), assuming the right-hand member zero. So that the complete solution to (4) is

$$c_1 = C_1 \sin pt + A e^{-\frac{k+h}{2} t} + B e^{-\frac{k-h}{2} t},$$

where

$$k = \frac{N r_1 + L r_2}{LN - M^2},$$

and

$$h = \frac{\sqrt{(N r_1 - L r_2)^2 + 4 r_1 r_2 M^2}}{LN - M^2}.$$

The constants A and B depend on the phase of the P.D. at the instant the coil is switched on. The exponential terms (since they are both real and negative) rapidly die away, so that practically $c_1 = C_1 \sin pt$ after a short time has elapsed. The same remarks apply to the value of c_2.

Hence

$$\tan \phi = \frac{\dfrac{b}{a} - \dfrac{p\mathrm{N}}{r_2}}{1 + \dfrac{bp\mathrm{N}}{ar_2}} = \frac{br_2 - ap\mathrm{N}}{ar_2 + bp\mathrm{N}} = \frac{p\mathrm{L} - \dfrac{p^3\mathrm{N}\mathrm{M}^2}{\mathrm{I}_2{}^2}}{r_1 + \dfrac{p^2 r_2 \mathrm{M}^2}{\mathrm{I}_2{}^2}} \cdot \cdot \quad (9)$$

From (9) it is evident that the difference in phase between the primary current and the P.D. is always diminished on closing the secondary, since, when the latter is open

$$\tan \phi = \frac{p\mathrm{L}}{r_1}.$$

In the same manner from (5) we obtain

$$\mathrm{C}_2 \sqrt{a^2 + b^2} \sin (pt + \theta + \psi) = -p\mathrm{ME} \cos (pt + \phi)$$
$$= p\mathrm{ME} \sin \left(pt + \phi + \frac{3\pi}{2}\right).$$

Hence
$$\mathrm{C}_2 = \frac{p\mathrm{ME}}{\sqrt{a^2 + b^2}}, \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (10)$$

and
$$\theta + \psi = \phi + \frac{3\pi}{2},$$

but
$$\psi = \phi + \chi.$$

Hence
$$\theta = \frac{3\pi}{2} - \chi = \pi + \left(\frac{\pi}{2} - \chi\right),$$

or θ is greater than π and less than $\frac{3\pi}{2}$. Also

$$\tan \theta = \cot \chi = \frac{r_2}{p\mathrm{N}} \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (11)$$

Now from equation (8),
$$\mathrm{C}_1 = \frac{\mathrm{E}}{\dfrac{\sqrt{a^2 + b^2}}{\mathrm{I}_2}}.$$

Call I the apparent impedance of the primary when the secondary is closed (I_1 is its impedance with secondary open). Then

$$\mathrm{I} = \frac{\sqrt{a^2 + b^2}}{\mathrm{I}_2},$$

or $\quad \mathrm{I}^2 \mathrm{I}_2{}^2 = a^2 + b^2$
$$= r_1{}^2 r_2{}^2 + p^4 (\mathrm{LN} - \mathrm{M}^2)^2 - 2p^2 r_1 r_2 (\mathrm{LN} - \mathrm{M}^2)$$
$$+ p^2 \mathrm{N}^2 r_1{}^2 + p^2 \mathrm{L}^2 r_2{}^2 + 2p^2 r_1 r_2 \mathrm{LN}$$
$$= \mathrm{I}_1{}^2 \mathrm{I}_2{}^2 - p^2 \mathrm{M}^2 \left\{ p^2 (2\mathrm{LN} - \mathrm{M}^2) - 2r_1 r_2 \right\},$$

or

$$I^2 = I_1^2 - \frac{p^2 M^2}{I_2^2} \{ p^2(2LN - M^2) - 2r_1 r_2 \} . \quad . \quad . \quad (12)$$

Equation (12) shows that I will only be less than I_1 when the quantity inside the brackets is positive; so that, if $2r_1 r_2 > p^2(2LN - M^2)$, I^2 is greater than I_1^2, and hence $I > I_1$, or the impedance of the primary is *increased* on closing the secondary.

For convenience let $\alpha_1 = \dfrac{pL}{r_1}$, and $\alpha_2 = \dfrac{pN}{r_2}$. α_1 is of course the tangent of the angle of lag of the primary current behind the P.D. when the secondary is unclosed, while $\dfrac{\pi}{2} + \tan^{-1}\alpha_2$ is the phase-angle between the primary and secondary currents when the secondary is closed.

Let $M = \beta \sqrt{LN}$, so that β represents the ratio of the magnetic induction passing through the secondary to that through the primary, and is of course less than unity, also $100(1-\beta)$ is the percentage magnetic leakage[*]. Substituting

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[*] This is only the case when the two coils are equal in dimensions and similar in shape; otherwise the ratio of the total lines of magnetic induction through the secondary to those through the primary, when a current flows in the primary, will not be the same as the ratio of the lines through the primary to those through the secondary when there is a current in the latter.

β is the geometrical mean of these two ratios. Thus: let n_1 be the number of turns in the primary and G_1 some constant depending on its shape and size, then the magnetic induction through the primary $= G_1 n_1^2$, and $L = G_1 n_1^2$. The induction through the secondary $= G_2 n_2$, and $N = G_2 n_2^2$, where the constant G_2 depends on the shape and size of the secondary. Let β_1 be the fraction of the primary induction that threads the secondary, and β_2 the fraction of the secondary induction that threads the primary. Then

$$M = G_1 n_1 \beta_1 n_2 = G_2 n_2 \beta_2 n_1.$$

Hence
$$M^2 = \beta_1 \beta_2 G_1 G_2 n_1^2 n_2^2,$$

or
$$M = \sqrt{\beta_1 \beta_2}\sqrt{LN};$$

so that
$$\beta = \sqrt{\beta_1 \beta_2}.$$

Also
$$G_1 \beta_1 = G_2 \beta_2, \text{ or } \frac{\beta_1}{\beta_2} = \frac{G_2}{G_1}.$$

So that for coils of the same shape and size

$$\beta_1 = \beta_2 = \beta, \text{ since } G_1 = G_2.$$

When the coils are of different shapes or sizes,

$$\frac{\beta_1}{\beta_2} = \frac{G_2}{G_1} = \frac{N}{L} \cdot \left(\frac{n_1}{n_2}\right)^2;$$

also if the number of turns in the primary and secondary is equal,

$$\frac{\beta_1}{\beta_2} = \frac{N}{L}.$$

these values in (12) it becomes

$$\left(\frac{I}{I_1}\right)^2 = 1 + \frac{\beta^2 \alpha_1 \alpha_2 \{2 - \alpha_1 \alpha_2 (2 - \beta^2)\}}{(1 + \alpha_1{}^2)(1 + \alpha_2{}^2)} \quad . \quad . \quad (13)$$

To make $\frac{I}{I_1}$ greater than unity, obviously

$$\alpha_1 \alpha_2 \text{ must be less than } \frac{2}{2 - \beta^2},$$

or the critical value of

$$\alpha_1 = \frac{2}{\alpha_2 (2 - \beta^2)} ; \ (\alpha_2 \text{ given}) ;$$

and that of

$$\alpha_2 = \frac{2}{\alpha_1 (2 - \beta^2)} ; \ (\alpha_1 \text{ given}).$$

When the primary and secondary are identical or have the same shape and coil-volume *, and the secondary when closed is short-circuited,

$$\alpha_1 = \alpha_2 = \alpha.$$

Then

$$\left(\frac{I}{I_1}\right)^2 = 1 + \frac{\beta^2 \alpha^2 \{2 - \alpha^2 (2 - \beta^2)\}}{(1 + \alpha^2)^2}, \quad . \quad . \quad (14)$$

and the critical value of $\alpha = \sqrt{\dfrac{2}{2 - \beta^2}}$.

When $\beta = 1$, or there is no magnetic leakage, the critical value of $\alpha = \sqrt{2}$.

To find the value of α_1 that will make $\frac{I}{I_1}$ a maximum, α_2 and β being given.

Obviously from (13) $\frac{I}{I_1}$ is a maximum when $\left(\dfrac{I}{I_1}\right)^2$ is a maximum, that is, when $\dfrac{\alpha_1 \{2 - \alpha_1 \alpha_2 (2 - \beta^2)\}}{1 + \alpha_1{}^2}$ is a maximum, since α_2 and β are constants.

Differentiating with respect to α_1 and equating to zero gives

$$\alpha_1 = \frac{\sqrt{4 + \alpha_2{}^2 (2 - \beta^2)^2} - \alpha_2 (2 - \beta^2)}{2}. \quad . \quad . \quad (15)$$

If $\beta = 1$, or there be no magnetic leakage,

$$\alpha_1 = \frac{\sqrt{4 + \alpha_2{}^2} - \alpha_2}{2} \ \text{ or } \ \frac{\alpha_1}{1 - \alpha_1{}^2} = \frac{1}{\alpha_2}. \quad . \quad (15\,a)$$

* Relative difference of thickness of insulation being supposed negligible, if different-sized windings are used.

If the coils have the same time-constants, or $\alpha_1 = \alpha_2 = \alpha$,

$$\alpha = \frac{1}{\sqrt{3-\beta^2}} \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (15\,b)$$

and

$$\frac{I}{I_1} = \sqrt{1 + \frac{\beta^2}{4-\beta^2}} = \frac{2}{\sqrt{4-\beta^2}};$$

if also $\beta = 1$,

$$\alpha = \frac{1}{\sqrt{2}}, \text{ and } \frac{I}{I_1} = \sqrt{1\cdot 3} = 1\cdot 155.$$

Obviously, if α_1 and β are known the value of α_2 that makes $\dfrac{I}{I_1}$ a maximum is by symmetry,

$$\alpha_2 = \frac{\sqrt{4 + \alpha_1^2(2-\beta^2)^2} - \alpha_1(2-\beta^2)}{2} \quad \text{or} \quad \frac{1-\alpha_2^2}{\alpha_2(2-\beta^2)} = \alpha_1,$$

or in the case of no magnetic leakage, $\dfrac{\alpha_2}{1-\alpha_2^2} = \dfrac{1}{\alpha_1}$.

If α_1 and α_2 are both variables, we have the two equations to be satisfied, viz.:—

$$\alpha_2 = \frac{1-\alpha_1^2}{\alpha_1(2-\beta^2)} \quad \text{and} \quad \alpha_1 = \frac{1-\alpha_2^2}{\alpha_2(2-\beta^2)},$$

$$\therefore \quad \alpha_1\alpha_2(2-\beta^2) = 1-\alpha_1^2 = 1-\alpha_2^2,$$

$$\therefore \quad \alpha_1 = \alpha_2 = \alpha \text{ say,}$$

and

$$\alpha = \frac{1-\alpha^2}{\alpha(2-\beta^2)} \quad \text{or} \quad \alpha = \frac{1}{\sqrt{3-\beta^2}}.$$

So that to get $\dfrac{I}{I_1}$ a maximum, the primary and secondary should have the same value of α, each equal to $\dfrac{1}{\sqrt{3-\beta^2}}$, or in the case of no magnetic leakage $= \dfrac{1}{\sqrt{2}}$; in which case $\dfrac{I}{I_1}$ will be $1\cdot 155$, or a $15\frac{1}{2}$ per cent. increase in impedance caused by short-circuiting the secondary, and this is the greatest that can be obtained.

Consider, then, the case of a transformer having coils with equal time-constants, and suppose there is no magnetic leakage.

For values of α below $\sqrt{2}$ the impedance is increased, and putting $\beta = 1$ in equation (14) gives

$$\frac{I}{I_1} = \frac{\sqrt{1+4\alpha^2}}{1+\alpha^2}.$$

From this equation curve I I I, Plate X., has been plotted; the abscissæ are values of α, and the ordinates values of $\dfrac{I}{I_1}$, expressed as percentages. For a transformer in which $\dfrac{L}{r_1} = \dfrac{N}{r_2} = \dfrac{1}{500}$ about, a second set of figures giving the frequency is also marked.

The curve CCC, Plate X., is the ratio of C the primary current when the secondary is closed to C_1 the same secondary open, and is evidently plotted from the equation

$$\frac{C}{C_1} = \frac{I_1}{I} = \frac{1 + \alpha^2}{\sqrt{1 + 4\alpha^2}}.$$

Power Distribution in above Transformer.

Let P be the power impressed on the primary when the secondary is closed ;

P_1 the same when the secondary is open ;

H the heat-power developed in the primary when the secondary is closed ;

P_2 the power developed in the secondary.

Then

$$P = \frac{p}{2\pi} \cdot \frac{E^2 I_2}{\sqrt{a^2 + b^2}} \int_0^{\frac{2\pi}{p}} \sin pt \cdot \sin (pt + \phi) \cdot dt$$

$$= \frac{E^2 (r_1 I_2^2 + r_2 p^2 M^2)}{2(a^2 + b^2)}$$

$$= \frac{E^2}{2r_1} \cdot \frac{1 + 2\alpha^2}{1 + 4\alpha^2}. \quad \cdots \quad (16)$$

$$H = \frac{p}{2\pi} \cdot \frac{E^2 I_2^2 r_1}{a^2 + b^2} \int_0^{\frac{2\pi}{p}} \sin^2 pt \cdot dt$$

$$= \frac{E^2 I_2^2 r_1}{2(a^2 + b^2)} = \frac{E^2}{2r_1} \cdot \frac{1 + \alpha^2}{1 + 4\alpha^2}. \quad \cdots \quad (17)$$

$$P_2 = \frac{p}{2\pi} \cdot \frac{(pME)^2 r_2}{a^2 + b^2} \int_0^{\frac{2\pi}{p}} \sin^2 (pt + \theta) \, dt$$

$$= \frac{p^2 M^2 E^2 r_2}{2(a^2 + b^2)} = \frac{E^2}{2r_1} \cdot \frac{\alpha^2}{1 + 4\alpha^2}. \quad \cdots \quad (18)$$

Obviously $P = P_2 + H$, unless there are masses of metal present, in which eddy currents are developed, or the frequency is so great that appreciable energy is radiated.

$$P_1 = \frac{p}{2\pi} \cdot \frac{E^2}{I_1^2} \int_0^{\frac{2\pi}{p}} \sin pt \cdot \sin (pt + \phi) \, dt$$

$$= \frac{E^2 r_1}{2 I_1^2} = \frac{E^2}{2 r_1} \cdot \frac{1}{1 + \alpha^2}. \qquad \cdots \cdots \quad (19)$$

Hence, from (16) and (19),

$$\frac{P}{P_1} = \frac{(1 + 2\alpha^2)(1 + \alpha^2)}{1 + 4\alpha^2} = \frac{1 + 3\alpha^2 + 2\alpha^4}{1 + 4\alpha^2}, \qquad \cdots \quad (20)$$

and from this equation (20) the curve marked PPP (Plate X.) is plotted.

The curves for P, H, P_2, and P_1 are plotted in Plate XI. for values of α up to 2.

Magnetizing Effect of the Coils.

Let g be the number of effective current-turns at any instant when the secondary is closed, and G its maximum value.

Then
$$g = n_1 c_1 + n_2 c_2,$$

where n_1 and n_2 are the number of turns in the primary and secondary respectively, and

$$G = \sqrt{n_1^2 C_1^2 + n_2^2 C_2^2 + 2 n_1 n_2 C_1 C_2 \cos \theta},$$

where θ is the phase-angle between the two currents.

If we assume the primary and secondary to occupy equal volumes, and we can neglect the relative difference in thickness of the insulation of the two coils, $\dfrac{n_1}{n_2} = \sqrt{\dfrac{r_1}{r_2}}$,

$$\therefore \ G = n_1 \sqrt{C_1^2 + C_2^2 \frac{r_2}{r_1} + 2 C_1 C_2 \sqrt{\frac{r_2}{r_1}} \cdot \cos \theta},$$

$$= \frac{n_1 E}{\sqrt{a^2 + b^2}} \sqrt{I_2^2 + p^2 M^2 \frac{r_2}{r_1} - 2 p^2 MN \sqrt{\frac{r_2}{r_1}}};$$

or (since M^2 is assumed $= LN$)

$$G = \frac{n_1 E r_2}{\sqrt{a^2 + b^2}} = \frac{n_1 E}{r_1 \sqrt{1 + 4\alpha^2}}.$$

Call G_1 the maximum value of g when the secondary is open; then

$$G_1 = \frac{n_1 E}{I_1} = \frac{n_1 E}{r_1 \sqrt{1 + \alpha^2}},$$

$$\therefore \quad \frac{G}{G_1} = \sqrt{\frac{1 + \alpha^2}{1 + 4\alpha^2}}. \quad . \quad . \quad . \quad . \quad (21)$$

Evidently, then, the magnetizing effect is always diminished on closing the secondary.

The curve GGG (Plate X.) is plotted from equation (21).

It will be seen, on inspecting Plate X., that in the cases of the impedance-curve and the current-curve the critical value for $\alpha = \sqrt{2} = 1 \cdot 414$, while the value of α that makes them a maximum and a minimum respectively is $\alpha = \frac{1}{\sqrt{2}} = \cdot 707$. This latter value of α is the critical value for the curve PPP, while, as may be seen by differentiating equation (20) and equating to zero, the value of α that makes this curve a minimum is $\frac{\sqrt{\sqrt{3} - 1}}{2}$, or $\cdot 4278$.

Consider, now, the case of primary and secondary having the same time-constants but with magnetic leakage.

Then we know the *critical value of* $\alpha = \sqrt{\frac{2}{2 - \beta^2}}$.

The value of α to make $\frac{I}{I_1}$ a maximum from (15b) $= \frac{1}{\sqrt{3 - \beta^2}}$.

Let γ represent the ratio of the former value of α to the latter, then

$$\gamma = \sqrt{\frac{6 - 2\beta^2}{2 - \beta^2}};$$

also the maximum value of $\frac{I}{I_1} = \frac{2}{\sqrt{4 - \beta^2}}$.

From equation (11),

$$\tan \theta = \frac{r_2}{pN} = \frac{1}{\alpha};$$

and θ is the angle by which the secondary current is in advance of the primary, and it lies between π and $\frac{3\pi}{2}$; it therefore follows that the angle by which the secondary current lags behind the primary lies between $\frac{\pi}{2}$ and π, and is $\frac{\pi}{2} + \tan^{-1} \alpha$. The following Table gives values of the above quantities for values of β from 1 to $\cdot 1$.

β.	Critical values of α.	Values of α for max. $\frac{I}{I_1}$.	γ.	Max. values of $\frac{I}{I_1}$.	Critical phase-angle.	Phase-angle for max. $\frac{I}{I_1}$.
1·0	$1·414 = \sqrt{2}$	$·707 = \frac{1}{\sqrt{2}}$	2	1·155	144° 44′	125° 16′
·9	1·300	·676	1·920	1·120	142 26	124 4
·8	1·210	·650	1·865	1·090	140 26	123 2
·7	1·150	·630	1·825	1·070	139 0	122 13
·6	1·105	·615	1·795	1·050	137 51	121 36
·5	1·070	·605	1·770	1·032	136 56	121 11
·4	1·045	·595	1·760	1·020	136 16	120 45
·3	1·023	·586	1·750	1·010	135 39	120 22
·2	1·010	·581	1·740	1·007	135 17	120 10
·1	1·002	·578	1·730	1·001	135 4	120 2

It will be seen from the column of values for γ that when $\beta = 1$, or there is no magnetic leakage, the critical value of α is twice its value for maximum $\frac{I}{I_1}$; and the effect of leakage is to diminish this number, so that when $\beta = ·1$ it is reduced to 1·73. This is shown in the subjoined figure.

Fig. 1.
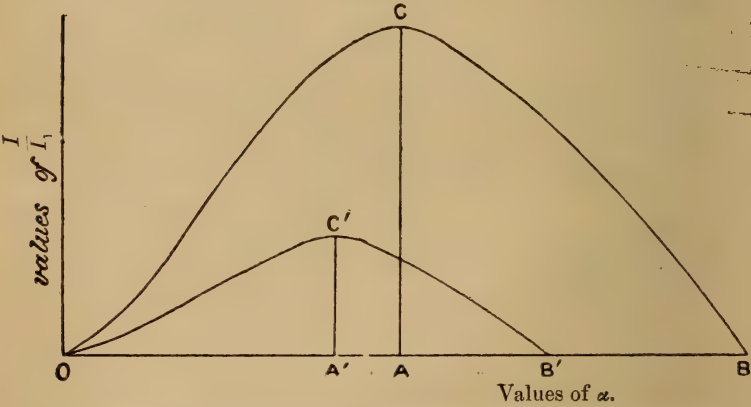
The curve OCB represents the critical part of the curve III (Plate X.) when there is no leakage, and A comes midway between O and B, so that $OA = \frac{1}{2} OB$; also $OB = \sqrt{2} = 1·414$, $OA = ·707$, and, if the point O represent 100 divisions, $AC = 15\frac{1}{2}$ divisions.

The curve OC′B′ represents the critical part when $\beta = ·1$; $OB′ = 1·002$ and $OA′ = ·578 = ·577 OB′$; also $A′C′ = ·12$ division. Hence we see that the effect of magnetic leakage

is to shift the point A′ corresponding to the maximum value of $\dfrac{I}{I_1}$ from midway between O and B′ and towards B′.

The author was enabled, through the kindness of Dr. Fleming, to try an experiment in the meter-testing room of the Electric Supply Company, using a Kelvin balance for measuring the currents through the primary coil. The alternating P.D. was obtained from the terminals of a transformer capable of giving over 100^A; and as the maximum current ever taken was $6\frac{1}{2}^A$ about, the P.D. may be assumed constant. The frequency was $83\cdot3$.

The air-core transformer used for the experiment consisted of two coils wound one inside the other, and of No. 20 B.W.G. cotton-covered wire. The inner coil was used as primary and the outer as secondary.

Each coil consisted of 5 layers, of 125 turns per layer.

Calculating the time-constants or values of $\dfrac{L}{R}$ for the coils by Perry's approximate formula, they worked out as $\cdot00121$ for the inner coil or primary, and $\cdot00152$ for the outer coil or secondary

$$p = 2\pi \times 83\cdot3 = 523.$$

Hence

$$\alpha_1 = \cdot00121 \times 523 = \cdot633,$$
$$\alpha_2 = \cdot00152 \times 523 = \cdot795.$$

The values of α_1 and α_2 were probably smaller than these values, as the coils became fairly warm from working; moreover the primary had the leads and the resistance of a Kelvin balance in series with it.

Take, then, α_1 as $\cdot5$, and α_2 as $\cdot7$.

The observed value of $\dfrac{I}{I_1}$ was $1\cdot032$.

Substituting these values in equation (13) makes $\beta = \cdot57$, or a magnetic leakage of 43 per cent., if the P.D. were a true sine function. This seems a rather large value for the leakage; and it is probable that the leakage was considerably less than this, but that the P.D. was not a pure sine function, and on this account the ratio $\dfrac{I}{I_1}$ was less than it otherwise would have been.

The above experiment was only a rough one, but it showed an increase of $3\cdot2$ per cent. in the impedance of the primary on closing the secondary : moreover the time-constants of the coils were not suited for giving the best effect with the

frequency employed; but, as is seen from the previous theoretical investigation, by employing a primary and a secondary having equal time-constants suitably related to the frequency, and a pure sine function P.D., an increase of impedance of from 10 to 12 per cent. ought to be obtained; $15\frac{1}{2}$ per cent. increase could never be obtained in practice, as there must always be some magnetic leakage.

In transformers with iron cores this effect would never be likely to escape notice as the values of $\frac{L}{R}$ would be so large that the critical frequency would be very small, so that for all frequencies employed in practice the impedance of the primary would diminish on closing the secondary. The iron core would also distort the current from a pure sine function.

XXXVI. *Graphic Representation of Currents in a Primary and a Secondary Coil.* By Prof. G. M. MINCHIN, *M.A.*[*]

IN this short paper is contained a solution of the following problem :—*A primary and a secondary coil occupy given positions; an alternating E.M.F., expressed by a sine function of the time, being applied to the primary, it is required to represent graphically the impedances and phases of the primary and secondary currents for all speeds of alternation.* (No iron cores employed.)

The occasion of this communication was a paper read to the Physical Society on the 27th of October, 1893, by Mr. Rimington, in which the subject was presented in a different manner.

Adopting the notation of Mr. Rimington's paper, let L, M, N, r_1, r_2 be, respectively, the coefficient of self-induction of the primary coil, the coefficient of mutual induction, that of self-induction of the secondary, and the resistances of the primary and secondary. Also let n be the frequency of the alternation, *i. e.* the number of alternations per second; $p = 2\pi n$; E = maximum value of the impressed E.M.F. Then, if the secondary coil is open (or $r_2 = \infty$), the impedance, I, of the primary is given by the expression

$$I_1 = \sqrt{r_1{}^2 + L^2 p^2}.$$

The impedance, I_2, of the secondary, if the primary were absent and the secondary plied by an alternating E.M.F.,

would be similarly given by the expression

$$I_2 = \sqrt{r_2{}^2 + N^2 p^2}.$$

Let p^2 be denoted by x, and, for shortness, let

$$a = r_1 r_2 - (LN - M^2)x,$$

$$b = (Nr_1 + Lr_2)\sqrt{x}.$$

Then, assuming that the E.M.F., namely e, applied to the primary is at any time, t, given by the equation

$$e = E \sin(pt + \phi),$$

the periodic parts, c_1 and c_2, of the currents at this time in the primary and secondary, respectively, are given by

$$c_1 = \frac{E I_2}{\sqrt{a^2 + b^2}} \sin pt,$$

$$c_2 = \frac{E M \sqrt{x}}{\sqrt{a^2 + b^2}} \sin(pt + \theta),$$

and we have

$$\theta = \tfrac{3}{2}\pi - \chi, \text{ where } \tan \chi = \frac{N\sqrt{x}}{r_2},$$

$$\phi = \psi - \chi, \text{ where } \tan \psi = \frac{b}{a}.$$

It thus follows that the actual impedances, I, I', of the primary and the secondary coil during the working of both are given by

$$I^2 = \frac{a^2 + b^2}{I_2{}^2}; \quad I'^2 = \frac{a^2 + b^2}{M^2 x}. \quad . \quad . \quad . \quad . \quad (1)$$

To represent I, I', and the phase-angles θ and ϕ graphically is the problem in hand. Take two rectangular axes, Ox, Oy, and along the first lay off the numerical values of p^2; then, taking $k^2 y$ to represent the value of I^2 corresponding to any value of p (or x), where k^2 is any constant which (according to the numerical values of L, M, N, &c.) may be required to confine the figure to any convenient size, we have

$$k^2 y = \frac{a^2 + b^2}{r_2{}^2 + N^2 x}, \quad . \quad . \quad . \quad . \quad . \quad (2)$$

or if for shortness we put $A^2 = LN - M^2$, and $B^2 = Nr_1 + Lr_2$,

$$k^2 y(N^2 x + r_2{}^2) = (r_1 r_2 - A^2 x)^2 + B^4 x ; \quad . \quad . \quad . \quad (3)$$

which equation denotes an hyperbola, ApQP, making an intercept, OA, on the axis of y such that

$$OA = \frac{r_1^2}{k^2}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

Call this curve the *primary hyperbola*.

In the same way, let I'^2 be denoted by $k^2 y'$; then

$$k^2 M^2 x y' = (r_1 r_2 - A^2 x)^2 + B^4 x, \quad . \quad . \quad . \quad (5)$$

showing that the values of I'^2 are also represented by the ordinates of an hyperbola, B H P'. We shall discuss this hyperbola more particularly, and show that it may be easily and rapidly drawn. Call it the *secondary hyperbola*. In the first place, it passes through the point $x = \dfrac{r_1 r_2}{A_2}$, $y' = \dfrac{B^4}{k^2 M^2}$; and the tangent at this point is parallel to Ox. The point is H,

whose ordinate we shall denote by h, so that

$$h = \frac{B^4}{k^2 M^2}. \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (6)$$

It is easily seen that both hyperbolas cut the axis of x in the same two points. These points are at the left of O and not shown, since negative values of x (i. e. p^2) do not belong to the physical problem. Moreover, the x of H is the geometric mean between the intercepts of the hyperbola on Ox.

Again, the centre of the hyperbola (6) is at the point C whose coordinates are

$$0 \quad \text{and} \quad \frac{N^2 r_1^2 + L^2 r_2^2 + 2 M^2 r_1 r_2}{k^2 M^2};$$

while one asymptote is Oy and the other is CS whose direction is easily known, since the tangent of its inclination to Ox is $\frac{A^4}{k^2 M^2}$.

Hence we have at once the asymptotes, Cy, CS and one point, H, of the hyperbola, from which the curve is rapidly drawn by the well-known rule that the parts intercepted between the curve and its asymptotes on every line drawn through H are equal. The other branch of this hyperbola is not represented, as it is irrelevant.

We shall now show that the primary hyperbola can be drawn from the secondary. Representing the values of I_1^2 and I_2^2 for all values of x by ordinates, so that $k^2 y_1 = I_1^2$, $k^2 y_2 = I_2^2$, we see that

$$k^2 y_1 = L^2 x + r_1^2, \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (7)$$
$$k^2 y_2 = N^2 x + r_2^2; \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (8)$$

so that the impedances are now represented by two right lines, AL and A′L′. (These are the impedances of the coils, each treated separately, as before explained.)

The primary line (7) passes, of course, through A, and always intersects the primary hyperbola in a point, Q, having a positive abscissa, viz.,

$$\frac{2 r_1 r_2}{2 LN - M^2},$$

which is < twice abscissa of H. Hence for some speed less than that represented by the abscissa of Q the ratio $\frac{I}{I_1}$ attains a maximum value. The point, p, representing this maximum value is easily found; for, no matter what curve AQP may be, if y is the ordinate of a point on it, and y_1 the corresponding ordinate of the right line AQ, the ratio $\frac{y}{y_1}$ is a maximum

at the point, p, of contact of a tangent to the curve drawn from the point where the right line AQ meets Ox.

Construct also the right line OT whose equation is

$$k^2\eta = \mathrm{M}^2 x ; \quad \cdots \quad \cdots \quad (9)$$

then, taking any value, ON, of x, draw the ordinate NP, and we have

$$y' = \mathrm{P'N} ; \quad y_2 = \mathrm{R'N} ; \quad y = \mathrm{PN} ; \quad \eta = \mathrm{VN}.$$

Moreover, it is obvious from the previous values that

$$\frac{y'}{y_2} = \frac{y}{\eta}, \quad \therefore y = \frac{y'}{y_2}\eta, \quad \cdots \quad \cdots \quad (10)$$

which shows that the point P on the primary hyperbola is deduced from the point P' on the secondary by the simple construction or calculation of a fourth proportional. (Though not belonging to the physical problem, it may be noted that one asymptote of the primary hyperbola is the parallel to Oy at the point where the secondary line, A'L', cuts Ox, the other asymptote making with Ox the angle whose tangent is $\frac{\mathrm{A}^4}{k^2\mathrm{N}^2}$.)

Finally, as regards the phase-angles, take χ first. We have $\tan\chi = \frac{\mathrm{N}\sqrt{x}}{r_2}$;

$$\therefore \sec^2\chi = \frac{\mathrm{I}_2^2}{r_2^2} = \frac{k^2 y_2}{r_2^2} = \frac{y_2}{\mathrm{OA''}},$$

$$\therefore \cos\chi = \sqrt{\frac{\mathrm{OA'}}{\mathrm{NR'}}}. \quad \cdots \quad \cdots \quad (11)$$

Hence, describing a circle on NR' as diameter, and drawing A'E parallel to Ox, meeting the circle in E, we have

$$\chi = \mathrm{ENR'};$$

$$\therefore \theta = \text{re-entrant angle ONE}.$$

Again, we have

$$\sin^2\psi = \frac{b^2}{a^2 + b^2} = \frac{b^2}{k^4\mathrm{M}^2 y' x} = \frac{b^2}{k^4\eta y'} = \frac{\mathrm{B}^4 x}{k^4\eta y'}.$$

But from (6), $h = \frac{\mathrm{B}^4 x}{k^4\eta}$;

$$\therefore \sin^2\psi = \frac{h}{y'}, \quad \cdots \quad \cdots \quad (12)$$

which shows that if we construct a circle on NP' as diameter, and take the point, D, in which this circle is cut by the tangent HD at H to the secondary hyperbola, we shall have

$$\psi = \mathrm{DN}x. \quad \cdots \quad \cdots \quad (13)$$

XXXVII. *An Apparatus to show, simultaneously to several hearers, the Blending of the Sensations of Interrupted Tones. By* ALFRED M. MAYER, *Ph.D.*[*]

IN the March number of this Journal, of the current year, I described several forms of apparatus used in my observations on the frequency of the interruptions of simple sounds required to blend these sounds and obtain from them continuous and uniform sonorous sensations. These experiments gave the data for the law connecting the pitch of a sound with the duration of its residual sensation.

The various apparatus described in that paper are, however, unsuited to exhibit the phenomena to more than one hearer at a time. To enable many hearers to observe the phenomena simultaneously, I have devised the apparatus shown in the figure.
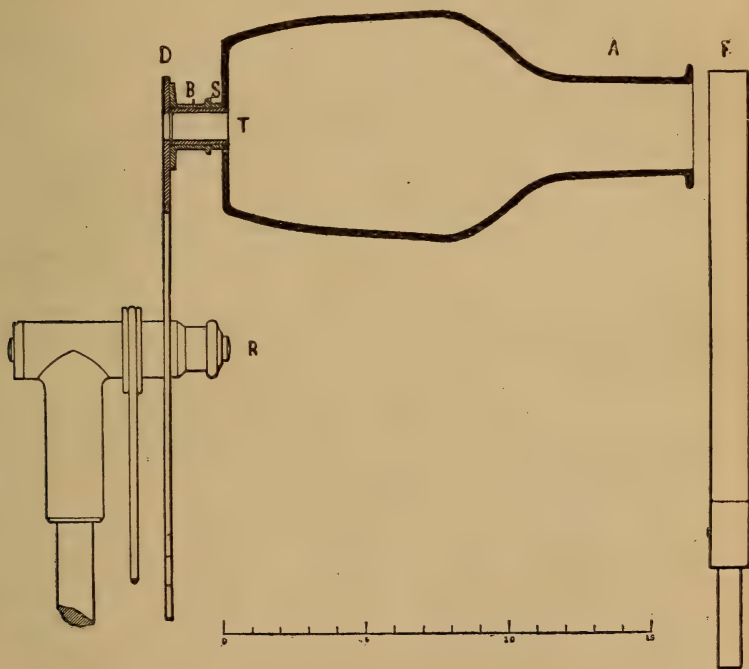
A brass tube, T, of 1·25 centim. interior diameter and 1·8 centim. long, is cemented in a hole in the bottom of the glass

* Communicated by the Author.

flask A ; which is a common form of flask, used by chemists. When the tube T is closed the air in the flask resounds powerfully to the sound of an UT_3 fork, F ; but when this tube is open, the resonator resounds so feebly as to be just audible at the distance of several feet from the flask.

If the tube be closed and opened several times in a second, we shall have loud explosions with faint interposed sounds. The opening and closing of the tube is effected by a perforated disk, D, revolving on a rotator, R. The tube T is placed in the circular path of the 16 holes which perforate the disk, with the mouth of the tube quite close to the surface of the disk. A short tube B, with flanges on it, slides neatly over the tube T, and the flange of B is pressed against the surface of the disk D by the helical spring S. By this arrangement the tube T is fully opened when a hole in the disk coincides with the opening of the tube, and is entirely closed when the flange of B is between the holes in the disk and gently pressing against its surface.

On slowly rotating the disk, while the fork is kept in vibration by an electromagnet, we have the perception of powerful beats which become more and more frequent as the velocity of rotation of the disk is increased till, with a certain velocity, the beats blend into a smooth continuous sound, which is that given by the fork when held near its proper resonator. This sound of UT_3 as given by the blending of its interrupted sounds is, however, accompanied by another and graver sound ; but the existence of this additional sound does not interfere with the clear perception of the blending of the interrupted sounds of UT_3. With this apparatus the blending of interrupted sounds has been shown to the entire satisfaction of a large audience.

To enable one readily to make the apparatus, the following dimensions are given. The diameter of opening of mouth of flask is 3 centim. Depth of flask, 16·25 centim. Capacity of flask, including tube T, 483 cubic centim.

In the figure the rotator, R, is shown driven by a cord. It is necessary, if an accurate determination is to be made of the duration of the residual sensation, to drive the disk by gearing as is done in the apparatus I have used. When the disk is driven by a cord one can show the blending of the interrupted sounds, but an accurate determination of the duration of the residual sensation is prevented by the friction which exists between the flange of B and the disk, though these surfaces are coated with a film of oil.

XXXVIII. *Notices respecting New Books.*

THE MEAN DENSITY OF THE EARTH : *an Essay to which the Adams Prize was adjudged in* 1893 *in the University of Cambridge.* By J. H. POYNTING, *Sc.D., F.R.S.* (Charles Griffin and Company.)

THE study of this work of Professor Poynting will be of the utmost value not only to anyone who proposes to engage on the special subject with which it deals, viz., the combined mathematical and experimental determination of the constant of gravitation—but also to the fairly large class of investigators who, in other experimental researches, have to deal with the measurement of extremely small quantities and with the action of disturbing influences both small and great. The chief value, indeed, of the Essay consists in the help which it affords in anticipating and allowing for such disturbances, and in the fairly complete historical *résumé* of the work which has been done, with the same object, by previous investigators.

A work of this kind would lose much of its value if it did not contain a fair record of failures as well as of successes ; and the author has not omitted to point out the defects which experiment from time to time revealed in his originally projected methods— as, for example, when in 1888, after he had supposed that the work was finished, he was led to suspect the existence of a tilting of the whole floor of the room in which his balance was placed by the moving of the large attracting mass from one position to another ; an unfortunate circumstance which necessitated the employment of a second attracting mass whose action was such as to diminish the effects which were to be observed.

The author is to be congratulated on the strictly scientific title under which he describes his work—" The Determination of the Mean Density of the Earth," or " The Determination of the Constant of Gravitation," instead of the utterly unmeaning " Determination of the *Weight* of the Earth," which is found in even such a work as Arago's ' Popular Astronomy,' and which is a characteristic of too much of our modern popular science *à la mode.* Have we not seen in some old and popular treatise a picture of " the room in which Mr. Baily *weighed* the Earth " ? It is to be hoped that some day our leading authorities will be induced to abandon that fatal dogma which is still, unfortunately, " of great emolument "— that *Science, to be popular, must, above all things, be inaccurate.*

We have said above that the chief value of the work consists in its helpfulness and suggestiveness, although it is tolerably certain that, with all the precautions which the author has taken to ensure success, the value which he has found for the mean density (viz. 5·493) must be very near the truth. He himself points out (p. 107) that with all apparatus the greater the size the greater are the errors produced by air-currents, a fact of which he was unaware when his apparatus was designed ; and that, if he were to start with a new design, he would certainly make the whole arrangement on a smaller scale—a great change which was advocated and justified by Professor Boys in a preliminary paper on the Cavendish experiment, read before the Royal Society in May 1889. There

is something amusing in the contrast between the dimensions of the apparatus used by Professors Poynting and Boys. Thus, the former uses two attracted spheres made of an alloy of lead and antimony, the masses (not quite equal) being each over $21\frac{1}{2}$ kilogrammes with diameters each nearly 16 centimetres, while one large attracting sphere has a mass of over 153 kilogrammes with a diameter of $30\frac{1}{2}$ centimetres, the other being of half the size; while of Professor Boys's apparatus it is sufficient to say that it is of the "waistcoat pocket" order of magnitude.

The author very justly summarizes his account of the previous methods for the determination of the mean density (those depending on plumb-line experiments, involving the calculation of the attraction of mountain masses, &c.), when he says (p. 39), "All this tends to confirm the conclusion that our knowledge of the distribution of the terrestrial matter is not yet sufficiently exact to enable us to obtain good values of the mean density of the Earth from the observed attraction of terrestrial masses. Rather must we assume the mean density from laboratory experiments, ...;" and of this latter kind are his own and those of Professor Boys. The former, or "Common Balance Method," may be roughly described as consisting in the suspension of two nearly equal heavy spheres from the ends of the arms of a common balance, while a very large attracting sphere is brought close under each of the former spheres successively, its attraction (chiefly on the sphere just above it) altering the position of equilibrium of the balance.

Incidentally (p. 78) Professor Poynting does a service to experimentalists in advocating the great value of what he calls "the double-suspension mirror method" of measuring small deflexions, as compared with the method of attaching the mirror to the moving needle commonly employed in electrometers and galvanometers, the latter multiplying the angular deflexion by 2 only, while the former, as employed by Professor Poynting, multiplied the angular deflexion of the balance by 150.

With a view to a second edition of this Essay, it may be well to point out a few things that might be altered with advantage. Doubtless, from the author's long familiarity with his symbols, he has not thought it worth while to notice that the symbols M and A in the mathematical investigation (pp. 109 &c.) are used each in two senses even in the same equation: at first they are, respectively, the mass of the large attracting sphere and the mass of one of the attracted spheres with a narrow diametral cylinder removed; while immediately afterwards (and in the same equation, end of p. 112) A stands for $\dfrac{M}{R}$, where now M means the "mass deflexion," and R the "rider deflexion." This is, for a time, somewhat confusing. Finally, a few misprints may be noted: line 16, p. 109, for n read n'; line 14, p. 110, for fig. 1 read fig. 17; line 1, p. 111, for $1-\dfrac{L}{2}$ read $l-\dfrac{L}{2}$; line 3, p. 115 brackets omitted in denominator at left side; together with a few others too obvious to escape notice.

XXXIX. *Proceedings of Learned Societies.*

GEOLOGICAL SOCIETY.

[Continued from vol. xxxvi. p. 594.]

November 22nd, 1893.—W. H. Hudleston, Esq., M.A., F.R.S.,
President, in the Chair.

THE following communications were read :—
1. 'The Basic Eruptive Rocks of Gran.' By W. C. Brögger,
Ord. Prof. of Min. and Geol. at the University of Christiania,
For. Memb. Geol. Soc.

In previous communications the author has maintained that the
different masses of eruptive rock which occur within the sunken
tract of country lying between Lake Mjösen and the Langesunds-
fjord are genetically connected, and have succeeded each other in a
regular order. The oldest rocks are the most basic, the youngest
(except the unimportant dykes of diabase) are the most acid, and
between the two extremes he has found a continuous series.

He is now preparing a detailed monograph on this series of
eruptive rocks, and in the present communication he gives an
account of the results of his work on the oldest members.

Several bosses of basic plutonic rock, now forming a series of
dome-shaped hills, lie along a north-and-south fissure-line. The
most northerly is that of Brandberget in the parish of Gran, about
50 or 60 kilometres N.N.W. of Christiania, and the most southerly
occurs at Dignaes on Lake Tyrifjord, about 35 kilom. W.N.W. of
the same town. The prevailing rock in these bosses is a medium
or coarse-grained olivine-gabbro-diabase ; but pyroxenites, horn-
blendites, camptonites, labrador-porphyrites, and augite-diorites also
occur. Analyses of the typical rocks from three localities on
the north-and-south line are given, and the conclusion is reached
that the average basicity of the rocks forming different bosses
decreases from north to south.

The contact-metamorphism is referred to ; and the presence of
hypersthene in the altered *Ogygia*-shales, coupled with its absence
from the same shales where they have been affected by quartz-
syenite, leads the author to the conclusion that the chemical nature
of the intrusive rock does, in certain cases, produce an influence on
the character of the metamorphism.

Innumerable dykes and sheets of camptonite and bostonite are
associated with the above-mentioned plutonic bosses. These are
regarded by the author as having been produced by differentiation
from a magma having the composition of the average olivine-gabbro-
diabase. Analyses are given, and it is proved that a mixture of nine
parts of the average camptonite and two of the average bostonite
would produce a magma having the composition of the average
olivine-gabbro-diabase. The petrographical variations, such as the
occurrence of pyroxenites and augite-diorites, in the plutonic masses
themselves are described, and attributed to differentiation under

physical conditions unlike those which gave rise to the camptonites and bostonites.

In discussing the general laws of differentiation the author points out that it must have taken place before crystallization to any extent had occurred, because there is a marked difference in mineralogical composition between the rocks occurring as bosses and those occurring as dykes; and, further, that it is dependent on the laws which determine the sequence of crystal-building, in so far as the compounds which, on given conditions, would first crystallize are those which have diffused to the cooling margin, and so produced a contact-stratum, of peculiar chemical composition, before any crystallization had taken place.

2. 'On the Sequence of Perlitic and Spherulitic Structures (a Rejoinder to Criticism).' By Frank Rutley, Esq., F.G.S.

This paper relates to the order in which the perlitic and spherulitic structures have been developed in a felsitic lava of Ordovician age from Long Sleddale, Westmoreland. The author having described this rock in a paper, published in the Quarterly Journal of the Society in 1884, and the accuracy of the views then expressed having been questioned, now endeavours to confirm his original statements, adducing in support fresh observations made upon this and other rocks of a similar kind.

3. 'Enclosures of Quartz in Lava of Stromboli, etc., and the Changes in Composition produced by them.' By Prof. H. J. Johnston-Lavis, M.D., F.G.S.

The author describes the existence of enclosures of quartz in a lava-stream at the Punta Petrazza on the east side of Stromboli, and also in the rock of the neck of Strombolicchio. He describes the effects of the rocks upon the enclosures, concluding that the quartz has undergone fluxion but not fusion, and has supplied silica to the containing lavas, thus causing an increase in the amount of pyroxene and a diminution in the amount of magnetite in the portions of those lavas that surround the inclusions and raising the percentage of silica. He suggests that such a process at greater depths and higher temperature may, under certain conditions, convert a basic rock into a more acid one, so that possibly the andesite of Strombolicchio may have been of basaltic character at an earlier period of its progress towards the surface. He offers the suggestion that other rocks or minerals once associated with the quartz have been assimilated by the magma.

December 6th, 1893.—W. H. Hudleston, Esq., M.A., F.R.S., President, in the Chair.

The following communications were read:—

1. 'The Purbeck Beds of the Vale of Wardour.' By the Rev. W. R. Andrews, M.A., F.G.S., and A. J. Jukes-Browne, Esq., B.A., F.G.S.

The authors have obtained better evidence than previously

existed for calculating the thicknesses of the several parts of the Purbeck series in the Vale of Wardour, and comparing the different subdivisions as developed in that Vale with those exposed in other localities. Putting together 22–24 feet of basement-beds of the Lower Purbeck strata seen in the Wockley section, 21 feet in Ridge Quarry, and 17 feet in Teffont Quarry, more than 60 feet of Lower Purbeck Beds are actually seen, and allowing for the gap between the Wockley and Ridge sections, 70 feet seems a fair estimate of the average thickness of the Lower Purbeck strata.

In the Teffont and Chicksgrove quarries, a little over 12 feet may be measured between the basal clay of the Middle Purbeck Beds and the Cinder Bed; while the great cutting on the Teffont line shows 19 feet of strata above the Cinder Bed, and the beds of Dinton cutting may be all on a higher horizon; so that an estimated thickness of 32 feet for the Middle Purbeck Beds is probably below the mark.

The clay and sand in the Dinton cutting must be 18–20 feet thick, and between its summit and the top of the second seam of calcareous grit there is a thickness of at least 8 feet. This grit forms the floor of Dinton Well, about 40 feet deep; hence there is a thickness of at least 66 feet of Upper Purbeck strata, and probably more than 2 and less than 12 feet in addition.

A comparison is instituted between the Purbeck Beds of the Vale of Wardour and those of the Dorset coast, etc., and some remarks are made upon the physical conditions under which the beds were deposited.

2. 'On a Picrite and other Associated Rocks at Barnton, near Edinburgh.' By Horace W. Monckton, Esq., F.L.S., F.G.S.

The object of this paper is to describe a cutting on a new railway in Barnton Park, where there is an excellent exposure of picrite. It consists of serpentinized olivine, augite, mica, iron oxide, and a little plagioclase-felspar, with a variable amount of interstitial matter. In many respects it comes very near to the picrite of Inchcolm, which island is $4\frac{1}{2}$ miles north of Barnton cutting. It differs from the picrite of Bathgate, and the probability is that the Barnton rock is an offshoot from the same magma as that which supplied the Inchcolm rock.

Besides the picrite other igneous rocks from the same cutting are described—in particular, a rock with porphyritic crystals of a green mineral replacing olivine, or more probably augite, and a great quantity of brown mica in small flakes and crystals. It is suggested that the name of mica-porphyrite might be given to this rock.

2. 'On a Variety of *Ammonites* (*Stephanoceras*) *subarmatus*, Young, from the Upper Lias of Whitby.' By Horace W. Monckton, Esq., F.L.S., F.G.S.

December 20th, 1893.—W. H. Hudleston, Esq., M.A., F.R.S.,
President, in the Chair.

The following communications were read:—

1. 'On the Stratigraphical, Lithological, and Palæontological
Features of the Gosau Beds of the Gosau District, in the Austrian
Salzkammergut.' By Herbert Kynaston, Esq., B.A.

This paper, after referring to the previous literature of the
subject, treats of the situation and physical aspects of the Gosau
Valley, the distribution of the Gosau Beds, their stratigraphy, palæ-
ontology, and geological horizon, and the physical conditions under
which they were deposited, and a comparison is instituted between
the Gosau Beds and the equivalent beds of other areas. The author
shows that Hippurites occur at two horizons in the Gosau Beds,—a
hippurite-limestone immediately above the basement-conglomerate
being characterized essentially by *Hippurites cornu-vaccinum*, which
is overlain by *Actæonella*- and *Nerinæa*-limestones and an estuarine
series, and above these is a second hippurite-limestone characterized
essentially by *Hippurites organisans*. It is pointed out that Toucas
similarly distinguishes two hippurite-zones in Southern France; the
lower, characterized essentially by *H. cornu-vaccinum*, being placed
by him at the top of the Turonian System, whilst the second, with
H. organisans, is referred to the summit of the Senonian; and the
author gives reasons for regarding the Gosau zones as the equiva-
lents of those of the South of France, in which case the Gosau Beds
will represent the uppermost Turonian and the whole of the Seno-
nian, *i. e.*, the zones of *Holaster planus, Micraster, Marsupites*, and
Belemnitella mucronata in England, whilst the upper unfossiliferous
beds may be the equivalents of the Danian Beds.

The strata are, on the whole, of shallow-water origin, and were
deposited in shallow bays in the Upper Cretaceous sea of Southern
and Central Europe, on the northern flanks of the Eastern Alps.
Probably towards the close of Upper Cretaceous times the southern
area of the Gosau District was cut off from the sea to form a lake-
basin in which the upper unfossiliferous series was deposited.

2. 'Artesian Boring at New Lodge, near Windsor Forest, Berks.'
By Prof. Edward Hull, M.A., LL.D., F.R.S., F.G.S.

The boring described in this paper was carried down from a level of
about 220 feet above Ordnance-datum, through the following beds:—

	feet
London Clay....................	} 214
Lower London Tertiaries	
Chalk	725
Upper Greensand.................	31
Gault	264
Lower Greensand	7

The Chalk was hard, and contained very little water; but on
reaching the Lower Greensand the water rose in the borehole to a
height of 7 feet from the surface.

The author discusses the probability of the Lower Greensand
yielding a plentiful water-supply in the Windsor district.

3. 'Boring on the Booysen Estate, Witwatersrand.' By D. Telford Edwards, Esq.

An account is given of a boring on the Booysen estate, situated about 2 miles from Johannesburg, and about 5000 feet south of the nearest point of outcrop of the 'Main Reef' of the Witwatersrand. The 'Bird-Reefs' crop out generally at a distance of 4000 feet south of the Main Reef.

The borehole, 1020 feet deep, passed through sandstones (often micaceous), quartzites, and conglomerates, the last-named having a collective thickness of 91 feet 7 inches, the two thickest reefs being respectively 26 and 22 feet thick. The dip of the beds was 35°. Traces of gold were obtained. All the reefs were highly mineralized, principally with iron-pyrites, and belonged to the 'Bird-Reef' series which overlies the Main Reef.

XL. *Intelligence and Miscellaneous Articles.*

MOLECULAR ENERGY OF GASES.

To the Editors of the Philosophical Magazine.

GENTLEMEN,

IT is a pity that Dr. Gore did not notice that the entries in the column on page 340, which he calls "square of molecular velocity," are nothing but a certain number (probably intended for 3395175) divided by the molecular weight of successive substances, and that when he multiplies the numbers in this column by the respective molecular weights again, the only ground for surprise is that the results do not come out identical. The numbers in his last column would in fact be all precisely the same were it not for a few arithmetical errors in the working.

Agreement to 4 figures (or to 7 for that matter) should always be suspected, especially since molecular weights themselves are not known accurately to 3 places. If Dr. Gore is still inclined to attribute importance to his figures, he may convince himself by inventing hypothetical substances with comic molecular weights and finding that they obey his law equally well.

As I understand him, however, he writes to request information as to what is known about molecular kinetic energy. A good deal is known; for instance the following :—

The mean square of molecular velocity is given for perfect gases by

$$p = \tfrac{1}{3}\rho u^2;$$

and since ρ varies as the molecular weight, for different gases at the same temperature, it follows that the average kinetic energies of the molecules of all permanent gases at the same temperature and pressure are the same.

But this statement does not hold for imperfect gases or vapours, because for them the external or applied pressure is not expressible so simply in terms of velocity, but is something more like

$$p = \tfrac{1}{3}\rho u^2 - \tfrac{2}{3}A\rho^2;$$

where the last term depends upon intermolecular forces, or what Clausius called the Virial, and Laplace denoted by K.

Besides this simple matter of separate gases, a much more interesting thing about mixed gases was discovered by Clerk Maxwell in 1860 (January, Phil. Mag.)—namely, that when a number of independent gases are thoroughly mixed in the same box, the average molecular kinetic energy of every variety of molecule is the same. This he found by direct mechanical reasoning, for he showed that at every encounter of unequal elastic spheres any initial or outstanding difference of energy was diminished by the collision; whence, since there are millions of collisions per second in ordinary gases, a condition of average uniformity of distribution of energy is soon attained.

From this law of Maxwell's the law of Avogadro, or a slight extension thereof, immediately follows; viz., that in any given volume of such a mixture, the number of molecules of each gas is proportional to that gas's individual pressure.

The proof is as follows:—$p = \frac{1}{3}nmu^2$, $mu^2 =$ const., therefore n varies with p; and this holds for every gas separately, provided that there are no intermolecular forces, chemical or other.

I am, Gentlemen,

Your obedient servant,

March 1, 1894.   OLIVER J. LODGE.

AN EXPERIMENT TO PHOTOGRAPH THE SPECTRUM OF LIGHTNING. BY G. MEYER.

In taking a photograph of the spectrum of lightning by means of a spectroscope provided with a slit, the difficulty is met with that, in order to obtain a satisfactory result, the lightning must be exactly in the prolongation of the optical axis of the apparatus. By the following arrangement this limitation may be removed. In front of the object-glass of the photographic apparatus arranged for parallel rays, a glass refraction-grating is fixed. An image of the lightning is then obtained on the plate, produced by the rays which traverse the grating without change of direction, and, on each side of this, images which owe their origin to the rays forming the lateral spectra. The number of images in each lateral spectrum is equal to the number of bright lines occurring in the spectrum of the lightning. During a storm at night in May of this year (1893) I made an experiment of this kind, for which a small hand camera was used; in front of the object-glass (an ordinary landscape-lens of 10 cm. focal distance) a glass grating of 0·0256 mm. breadth of grating, was fixed. Two plates were exposed. The first shows two flashes, and right and left of each of them an image which corresponds to the lateral spectrum of the first order. In the present case this only contains one line. On the second plate were more flashes, and in the immediate neighbourhood of the horizon, above which projected roofs of houses with various chimneys. Between the chimneys a strong flash is to be observed, with its two lateral spectra. I measured the angle

between the edges of two chimneys and the photographic apparatus, and found it to be 2° 46′ 55″. By means of a cathetometer the distance of corresponding parts of the flash and of the lateral spectra, and the distance of the edges of the chimneys, were measured. The first magnitude was 1·6 mm. and the second 5·2. From these data the angle of diffraction is calculated at $0°·856$, and the wave-length at $382 . 10^{-6}$ mm. The determination of the angle of diffraction is independent of a knowledge of the focal distance of the object-glass, and of possible misdrawing.

This measurement is not accurate enough to determine to what body this line belongs; it can only be concluded from this that that portion of the light which is chiefly effective in photographing lightning-flashes has approximately the wave-length $382 . 10^{-6}$.

This communication has been made with a view of inciting other observers, who have at their disposal better apparatus and can more frequently observe storms, to make experiments by this method. It is possible that additional ultra-violet lines may be established if we succeed in photographing flashes at several hundred metres distance, for in the present case the distance of the storm was more than 10 km.

Measurements of the wave-lengths of lines of the spectrum of lightning have been made by Vogel and by Schuster, by means of a spectrum apparatus provided with a slit. The following table gives the wave-lengths arrived at in their experiments :—

Schuster.	H. C. Vogel.
568·1	
559·2	
533·4	534·1
526·0	
518·2	518·4
500·2	500·2
	486·0
	458·3
	467·3

To this must be added one in the ultra-violet part of the spectrum of the approximate value of $382 . 10^{-6}$.—Wiedemann's *Annalen,* Feb. 1894.

ON THE MAGNETIZATION OF SOFT IRON.
BY M. P. JOUBIN.

In a note in the number of this Journal for last month I have shown that we may expect to find a *characteristic equation* of the intensity of magnetization of strongly magnetic bodies as a function of the susceptibility, and I proposed to verify this conclusion experimentally. But the experiments of Rowland * solve this question, at any rate for the bodies investigated by him, and which comprise different varieties of iron, steel, and nickel.

* Phil. Mag. 4th series, vol. xlvi. p. 140.

There is a characteristic equation with coefficients independent of the nature of the body; consequently, *the theorem of corresponding states applies to magnetism.*

Let us imagine an ideal magnetic body for which the susceptibility corresponding to an infinitely small field vanishes, and for which the maximum intensity of magnetization I_m is exactly equal to three times the critical intensity I_c. The curve representing the intensity I as a function of K is a parabola, and by referring the variables to their critical values I_c and K_c, the *reduced equation* of the parabola may be written, as is readily seen,

$$\left(x = \frac{I}{I_c}, \; y = \frac{K}{K_c}\right)$$

$$x = 1 + \tfrac{1}{2}(1-y) \pm \tfrac{3}{2}\sqrt{1-y}.$$

This is an ideal case, for :—

I. The susceptibility has a finite value K_0 when the field vanishes :

II. The value I_0 of I corresponding to K_0 is not equal to $3I_c$.

But to obtain the same conditions, let us measure the susceptibility, not from 0, but from K_0, and take the ratio $\dfrac{K - K_0}{K_c - K_0}$. If we construct curves for Rowland's experiments, it will be seen that $\dfrac{I_0}{I_c}$ is very appreciably constant for all substances and is equal to 2·66. It follows from this by a simple calculation that the *characteristic equation* is

$$\left(x = \frac{I}{I}, \; y = \frac{K - K_0}{K_c - K_0}\right)$$

$$x = 1 + 0.33(1-y) \pm 1.3\sqrt{1-y}.$$

The following are some examples showing the agreement of this formula with experiments :—

I. Soft Iron : $4\pi K_0 = 180$; $I_c = 500$; $4\pi K_c = 2460$.

	I'.		I''.	
$4\pi K$.	Calc.	Obs.	Calc.	Obs.
650	1211	1230	54	50
1500	993	985	147·5	150
2000	825	810	241·5	250

II. Soft Iron : $4\pi K_0 = 320$; $I_c = 520$; $4\pi K_c = 4700$.

850	1300	1290	41	35
2000	1151	1140	99	100·5
3600	900	885	226	240
4320	731	721	350	360

III. Nickel : $4\pi K_0 = 30$; $I_c = 165$; $4\pi K_c = 170$.

	I′.		I″.	
$4\pi K$.	Calc.	Obs.	Calc.	Obs.
50	41	42·5	13	10
100	35·2	34·5	50	45
150	25·2	25	90	90

IV. Steel : $4\pi K_0 = 50$; $I_c = 570$; $4\pi K_c = 320$.

250	986	960	245	245

V. Soft Iron : $4\pi K_0 = 300$; $I_c = 520$; $4\pi K_c = 3550$.

1000	1240	1200	60	50
2000	1060	1030	135	140
3000	816	816	276	290

—*Communicated by the Author,* from the *Comptes Rendus,* Jan. 15, 1894.

ERRATUM in last paper.   P. 337, line 7 from bottom, p. 338, line 2 from top, *for* H_m *read* $I \times I_m$.

ON THE THERMAL BEHAVIOUR OF LIQUIDS.

To the Editors of the Philosophical Magazine.

GENTLEMEN,

In the February number of the Philosophical Magazine, Professors Ramsay and Young have published a short paper on the thermal behaviour of liquids, in which the results of some of my experiments are attacked. In the interest of true knowledge I cannot leave these remarks unnoticed, as I consider they rest on an insufficient foundation.

The principal remark concerning the defectiveness of the arrangements employed to obtain constant high temperatures does not apply to me, as the authors of the above-named paper may easily see. In my article (Wied. *Ann.* l. p. 529, 1893) I expressly and clearly state that in the glycerine bath which contained the experimental tubes the temperature was perfectly uniform and could be maintained constant for hours. This I proved by repeated experiments.

The conclusions arrived at by the authors and stated on p. 207 (Phil. Mag. vol. xxxvii. 1894) are in accord with my own observations, for I also found that when the experimental tubes were uniformly heated in the glycerine bath no striæ were visible, but only a rusty appearance. As regards the purifying of the liquid from air, the authors may see what particular pains were taken by referring to p. 530 of my article.   B. GALITZINE.

St. Petersburg : Physical Laboratory
    of the Academy of Sciences,
        February 21, 1894.

ON THE THERMAL BEHAVIOUR OF LIQUIDS.
BY P. DE HEEN.

To the Editors of the Philosophical Magazine.

GENTLEMEN,

In the February number of this Journal Messrs. Ramsay and Young have published a note on the critical temperature in which a statement appears of which, in the interests of science, I am compelled to ask them for an explanation; they have characterized as "very inaccurate" a paper on the same subject by myself[*]. This would not be of much importance if my work had not attracted the attention of many physicists and especially of M. Galitzine, who would thus have been led into error by my mistake.

To avoid this I venture respectfully to request Profs. Ramsay and Young to point out the errors of reasoning and of experimentation that I have made in the demonstration of my fundamental proposition :—" *The volume of a fluid is not always defined by the temperature and pressure only ;*" *thus fluids of different density can correspond to the same temperature and pressure.* On this proposition all my deductions rest.

It would also be of service to show the error committed by M. Galitzine in his demonstration.

I may also point out to Profs. Ramsay and Young that before 1880 I had arrived at the conclusion that the particles that constitute liquids have a different volume from the particles of vapour. It was by this means that I explained the maximum density of water[†].

Profs. Ramsay and Young think with M. Gouy that the only variation of density produced in liquids confined in a tube results from the variation of hydrostatical pressure; the great compressibility of fluids near the critical point would cause very considerable variations of density. The ingenious interpretation of M. Gouy, which would explain very simply an anomaly that at first had a paradoxical appearance, cannot now unhappily be admitted. If it were correct there should be produced *immediately,* at the critical temperature, a stable equipoise in a pipe vertically fixed. The experiments I published last year show that this is not the case; thus the mode of distribution of substance is different a little after the disappearance of the meniscus and twenty-four hours after[‡].

P. DE HEEN.

[*] " Sur un état de la matière caractérisé par l'indépendance de la pression et du volume spécifique," *Bulletin de l'Acad. Roy. de Belgique*, t. xxiv. for 1892.

[†] " De la dilatabilité de quelques liquides organiques et des solutions salines," *présenté à l'Acad. Roy. de Belgique*, May 6, 1879.

[‡] " De l'influence du temps sur le mode de formation du ménisque à la température de transformation," *Bull. de l'Acad. Roy. de Belgique* [3] xxv. p. 14 (1893).

XLI. *The Internal Work of the Wind.*
By S. P. Langley [*].

[Plates V.–IX.]

Part I.—*Introductory.*

IT has long been observed that certain species of birds maintain themselves indefinitely in the air by " soaring," without any flapping of the wing or any motion other than a slight rocking of the body ; and this, although the body in question is many hundred times denser than the air in which it seems to float with an undulating movement, as on the waves of an invisible stream.

No satisfactory mechanical explanation of this anomaly has been given, and none would be offered in this connexion by the writer, were he not satisfied that it involves much more than an ornithological problem, and that it points to novel conclusions of mechanical and utilitarian importance. They are paradoxical at first sight, since they imply that under certain specified conditions very heavy bodies entirely detached from the earth, immersed in, and free to move in, the air, can be sustained there indefinitely, without any expenditure of energy from within.

These bodies may be entirely of mechanical construction,

as will be seen later, but for the present we will continue to consider the character of the invisible support of the soaring bird, and to study its motions, though only as a pregnant instance offered by nature to show that a rational solution of the mechanical problem is possible.

Recurring, then, to the illustration just referred to, we may observe that the flow of an ordinary river would afford no explanation of the fact that nearly inert creatures, while free to move, although greatly denser than the fluid, yet float upon it ; which is what we actually behold in the aerial stream, since the writer, like others, has satisfied himself by repeated observation that the soaring vultures and other birds appear as if sustained by some invisible support, in the stream of air, sometimes for at least a considerable fraction of an hour. It is frequently suggested by those who know these facts only from books, that there must be some quivering of the wings, so rapid as to escape observation. Those who do know them from observation are aware that it is absolutely certain that nothing of the kind takes place, and that the birds sustain themselves on pinions which are quite rigid and motionless, except for a rocking or balancing movement involving little energy.

The writer desires to acknowledge his indebtedness to that most conscientious observer, M. Mouillard *, who has described these actions of the soaring birds with incomparable vividness and minuteness, and who asserts that they, under certain circumstances, without flapping their wings, rise and actually advance against the wind.

To the writer, who has himself been attracted from his earliest years to the mystery which has surrounded this action of the soaring bird, it has been a subject of continual surprise that it has attracted so little attention from physicists. That nearly inert bodies, weighing from 5 to 10, and even more, pounds, and many hundred times denser than the air, should be visibly suspended in it above our heads, sometimes for hours at a time, and without falling,—this, it might seem, is, without misuse of language, to be called a physical miracle ; and yet the fact that those whose province it is to investigate nature have hitherto seldom thought it deserving attention is perhaps the greater wonder.

This indifference may be in some measure explained by the fact that the largest and best soarers are of the vulture kind, and that their most striking evolutions are not to be seen in those regions of the Northern Temperate Zone where the majority of those whose training fits them to study the sub-

* L. P. Mouillard, *L'Empire de l'Air*, Paris : G. Masson.

ject are found. Even in Washington, however, where the writer at present resides, scores of great birds may be seen at times in the air together, gliding with and against the wind, and ascending higher at pleasure, on nearly motionless wings. " Those who have not seen it," says M. Mouillard, " when they are told of this ascension without the expenditure of energy, are always ready to say, ' but there must have been movements, though you did not see them;' " "and in fact," he adds, " the casual witness of a single instance, himself, on reflection, feels almost a doubt as to the evidence of his senses, when they testify to things so extraordinary."

Quite agreeing with this, the writer will not attempt any general description of his own observations, but as an illustration of what can sometimes be seen, will give a single one, to whose exactness he can personally witness. The common " Turkey Buzzard " (*Cathartes aura*) is so plentiful around the environs of Washington that there is rarely a time when some of them may not be seen in the sky, gliding in curves over some attractive point, or, more rarely, moving in nearly straight lines on rigid wings, if there be a moderate wind. On the only occasion when the motion of one near at hand could be studied in a very high wind, the author was crossing the long " Aqueduct Bridge " over the Potomac, in an unusually violent November gale, the velocity of the wind being probably over 35 miles an hour. About one third of the distance from the right bank of the river, and immediately over the right parapet of the bridge, at a height of not over 20 yards, was one of these buzzards, which, for some object which was not evident, chose to keep over this spot, where the gale, undisturbed by any surface irregularities, swept directly up the river with unchecked violence. In this aerial torrent, and apparently indifferent to it, the bird hung, gliding in the usual manner of its species, round and round, in a small oval curve, whose major axis (which seemed toward the wind) was not longer than twice its height from the water. The bird was therefore at all times in close view. It swung around repeatedly, rising and falling slightly in its course, while keeping, as a whole, on one level, and over the same place, moving with a slight swaying, both in front and lateral direction, but in such an effortless way as suggested a lazy yielding of itself to the rocking of some invisible wave.

It may be asserted that there was not only no flap of the wing, but not the quiver of a wing-feather visible to the closest scrutiny, during the considerable time the bird was under observation, and during which the gale continued. A record of this time was not kept, but it at any rate lasted until

the writer, chilled by the cold blast, gave up watching and moved away, leaving the bird still floating about, at the same height in the torrent of air, in nearly the same circle, and with the same aspect of indolent repose.

If the wind is such a body as it is commonly supposed to be, it is absolutely impossible that this sustention could have taken place in a horizontal current any more than in a calm, and yet that the ability to soar is, in some way, connected with the presence of the wind, became to the writer as certain as any fact of observation could be, and at first the difficulty of reconciling such facts (to him undoubted) with accepted laws of motion seemed quite insuperable.

Light came to him through one of those accidents which are commonly found to occur when the mind is intent on a particular subject, and looking everywhere for a clue to its solution.

In 1887, while engaged with the "whirling-table" in the open air at the Allegheny Observatory, he had chosen a quiet afternoon for certain experiments, but in the absence of the entire calm, which is almost never realized, had placed one of the very small and light anemometers made for hospital use in the open air, with the object of determining and allowing for the velocity of what feeble breeze existed. His attention was called to the extreme irregularity of this register, and he assumed at first that the day was more unfavourable than he had supposed. Subsequent observations, however, showed that when the anemometer was sufficiently light and devoid of inertia, the register always showed great irregularity, especially when its movements were noted, not from minute to minute, but from second to second.

His attention once aroused to these anomalies, he was led to reflect upon their extraordinary importance in a possible mechanical application. He then designed certain special apparatus hereafter described, and made observations with it which showed that "wind" in general was not what it is commonly assumed to be—that is, air put in motion with an approximately uniform velocity in the same strata ; but that, considered in the narrowest practical sections, wind was always not only not approximately uniform, but variable and irregular in its movements beyond anything which had been anticipated, so that it seemed probable that the very smallest part observable could not be treated as approximately homogeneous, but that even here there was an internal motion to be considered, distinct both from that of the whole body and from its immediate surroundings. It seemed to the writer to follow as a necessary consequence, that there might be a

potentiality of what may be called " internal work " * in the wind.

On further study, it seemed to him that this internal work might conceivably be so utilized as to furnish a power which should not only keep an inert body from falling, but cause it to rise, and that while this power was the probable cause of the action of the soaring bird, it might be possible through its means to cause any suitably disposed body, animate or inanimate, wholly immersed in the wind and wholly free to move, to advance against the direction of the wind itself. By this it is not meant that the writer then devised means for doing this, but that he then attained the conviction both that such an action involved no contradiction of the laws of motion, and that it was mechanically possible (however difficult it might be to realize the exact mechanism by which this might be accomplished).

It will be observed that in what has preceded it is intimated that the difficulties in the way of regarding this even in the light of a theoretical possibility may have proceeded, with others as with the writer, not from erroneous reasoning, but from an error, in the premises, entering insidiously in the form of the tacit assumption made by nearly all writers, that the word " wind " means something so simple, so readily intelligible, and so commonly understood, as to require no special definition ; while, nevertheless, the observations which are presently to be given show that it is, on the contrary, to be considered as a generic name for a series of infinitely complex and little-known phenomena.

Without determining here whether any mechanism can be actually devised which shall draw from the wind the power to cause a body wholly immersed in it to go against the wind, the reader's consideration is now first invited to the evidence that there is no contradiction to the known laws of motion, and at any rate no theoretical impossibility in the conception of such a mechanism, if it is admitted that the wind is not what it has been ordinarily taken to be, but what the following observations show that it is.

What immediately follows is an account of evidence of the complex nature of the " wind," of its internal movements, of

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* Since the term " internal work " is often used in thermodynamics to signify molecular action, it may be well to observe that it here refers not to molecular movements, but to pulsations of sensible magnitude, always existing in the wind, as will be shown later, and whose extent and extraordinary possible mechanical importance it is the object of this research to illustrate. The term is so significant of the author's meaning, that he permits himself the use of it here, in spite of the possible ambiguity.

the resulting potentiality of this internal work, and of attempts which the writer has made to determine quantitatively its amount by the use of special apparatus, recording the changes which go on (so to speak) *within* the wind in very brief intervals. These results may, it is hoped, be of interest to meteorologists, but they are given here with special reference to their important bearing on the future of what the writer has ventured to call the science of Aerodromics *.

The observations which are first given were made in 1887 at Allegheny, and are supplemented by others made at Washington in the present year †.

What has just been said about their possible importance will perhaps seem justified, if it is remarked (in anticipation of what follows later) that the result of the present discussion implies not only the theoretical, but the mechanical possibility, that a heavy body wholly immersed in the air, and sustained by it, may without the ordinary use of wind, or sail, or steam, and without the expenditure of any power except such as may be derived from the ordinary winds, make an aerial voyage in any direction, whose length is only limited by the occurrence of a calm. A ship is able to go against a head wind by the force of that wind, owing to the fact that it is partly immersed in the water which reacts on the keel, but it is here asserted that (contrary to usual opinion and in opposition to what at first may seem the teachings of physical science) it is not impossible that a heavy and nearly inert body *wholly* immersed in the air can be made to do this.

The observations on which the writer's belief in this mechanical possibility are founded will now be given.

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* From ἀεροδρομέω, to traverse the air ; ἀεροδρόμος, an air-runner.

† It will be noticed that the fact of observation here is not so much the movement of currents, such as the writer has since learned was suggested by Lord Rayleigh so long ago as 1883, still less of the movement of distinct currents at a considerable distance above the earth's surface, but of what must be rather called the effect of the irregularities and pulsations of any ordinary wind, within the immediate field of examination, however narrow.

See the instructive article by Lord Rayleigh in ' Nature,' April 5, 1883. Lord Rayleigh remarks that continued soaring implies " (1) that the course is not horizontal, (2) that the wind is not horizontal, or (3) that the wind is not uniform." " It is probable," he says, " that the truth is usually represented by (1) or (2) ; but the question I wish to raise is whether the cause suggested by (3) may not sometimes come into operation,"

PART II.— *Experiments with the use of special apparatus.*

In the ordinary uses of the anemometer (let us suppose it to be a Robinson's anemometer, for illustration) the registry is seldom taken as often as once a minute ; thus, in the ordinary practice of the United States Weather Bureau, the registration is made at the completion of the passage of each mile of wind. If there be very rapid fluctuations of the wind, it is obviously desirable, in order to detect them, to observe the instrument at very brief intervals, *e. g.* at least every second, instead of every minute or every hour, and it is equally obvious that in order to take up and indicate the changes which occur in these brief intervals, the instrument should have as little inertia as possible, its momentum tending to falsify the facts, by rendering the record more uniform than would otherwise be the case.

In 1887 I made use of the only apparatus at command— an ordinary small Robinson's anemometer, having cups 3 inches (7·5 centim.) in diameter, the centres of the cups being 6¾ inches (16¾ centim.) from the centre of rotation. This was placed at the top of a mast 53 feet (16·2 metres) in height, which was planted in the grounds of the Allegheny Observatory, on the flat summit of a hill which rises nearly 400 feet (122 metres) above the valley of the Ohio River. It was, accordingly, in a situation exceptionally free from those irregularities of the wind which are introduced by the presence of trees and of houses, or of inequalities of surface.

Every twenty-fifth revolution of the cups was registered by closing an electric circuit, and the registry was made on the chronograph of the Observatory by a suitable electric connexion, and these chronograph sheets were measured and the results tabulated. A portion of the record obtained on July 16, 1887, is given on Plate V., the abscissæ representing time, and the ordinates wind velocities. The observed points represent the wind's velocities as computed from the intervals between each successive electrical contact, as measured on the chronograph sheets, and for convenience in following the succession of observed points they are here joined by straight lines, though it is hardly necessary to remark that the change in velocity is in fact, though quite sharp, yet not in general discontinuous, and the straight lines here used for convenience do not imply that the rate of change of velocity is uniform.

The wind velocities during this period of observation ranged from about 10 to 25 miles an hour, and the frequency of measurement was every 7 to 17 seconds. If, on the one hand,

owing to the weight and inertia of the anemometer, this is far from doing justice to the actual irregularities of the wind, on the other it equally shows that the wind was far from being a body of even approximate uniformity of motion, and that even when considered in quite small sections, the motion was found to be irregular almost beyond conception—certainly beyond anticipation; for this record is not selected to represent an extraordinary breeze, but the normal movement of an ordinary one.

By an application of these facts, to be presented later, I then reached by these experiments the conclusion that it was theoretically possible to cause a heavy body wholly immersed in the wind to be driven in the opposite direction, *e. g.* to move east while the wind was blowing west, without the use of any power other than that which the wind itself furnished, and this even by the use of plane surfaces, and without taking advantage of the more advantageous properties of curved ones.

This power, I further already believed myself warranted by these experiments in saying, could be obtained by the movements of the air in the horizontal plane alone, even without the utilization of currents having an upward trend. But I was obliged to turn to other occupations, and did not resume these interesting observations until the year 1893.

Although the anemometer used at Allegheny served to illustrate the essential fact of the rapid and continuous fluctuations of even the ordinary and comparatively uniform wind, yet owing to the inertia of the arms and cups, which tended to equalize the rate (the moment of inertia was approximately 40,000 gr. cm.^{2}), and to the fact that the record was only made at every twenty-fifth revolution, the internal changes in the horizontal component of the wind's motion, thus representing its potential work, were not adequately recorded.

In January 1893 I resumed these observations at Washington with apparatus with which I sought to remedy these defects, using as a station the roof of the north tower of the Smithsonian Institution building, the top of the parapet being 142 feet (43·3 metres) above the ground, and the anemometers, which were located above the parapet, being 153 feet (46·7 metres) above the ground. I placed them in charge of Mr. George E. Curtis, with instructions to take observations under the conditions of light, moderate, and high winds. The apparatus used was, first, a Weather Bureau Robinson anemometer of standard size, with aluminium cups. Diameter to centre of cups 34 cm.; diameter of cups 10·16 cm.; weight of arms and cups 241 grams; approximate moment of inertia 40,710 gr. cm.^{2}

A second instrument was a very light anemometer, having paper cups, of standard pattern and diameter, the weight of arms and cups being only 74 grams, and its moment of inertia 8604 gr. cm.^{2}

With this instrument a number of observations were taken, when it was lost by being blown away in a gale. It was succeeded in its use by one of my own construction, which was considerably lighter. This was also blown away. I afterwards employed one of the same size as the standard pattern, weighing 48 grams, having a moment of inertia of 11,940 gr. cm.^{2}; and, finally, I constructed one of half the diameter of the standard pattern, employing cones instead of hemispheres, weighing 5 grams, and having a moment of inertia of but 300 gr. cm.^{2}

In the especially light instruments the electric record was made at every half revolution, on an ordinary astronomical chronograph, placed upon the floor of the tower, connected with the anemometer by an electric circuit. Observations were made on January 14, 1893, during a light wind having a velocity of from 9 to 17 miles an hour; on January 25 and 26 during a moderate wind, having a velocity of from 16 to 28 miles an hour; and on February 4 and 7, during a moderate and high wind ranging from 14 to 36 miles an hour. Portions of these observations are given on Plates VI., VII., and VIII. A short portion of the record obtained with the standard Weather Bureau anemometer during a high north-west wind is given on Plate IX.

A prominent feature presented by these diagrams is that the higher the absolute velocity of the wind, the greater the relative fluctuations which occur in it. In a high wind the air moves in a tumultuous mass, the velocity being at one moment perhaps 40 miles an hour, then diminishing to an almost instantaneous calm, and then resuming [*].

The fact that an absolute local calm can momentarily occur during the prevalence of a high wind was vividly impressed upon me during the observations of February 4, when, chancing to look up to the light anemometer, which was revolving so rapidly that the cups were not separately distinguishable, I saw them completely stop for an instant, and then resume their previous high speed of rotation, the whole within the fraction of a second. This confirmed the suspicion that the chronographic record, even of a specially light anemometer, at most but imperfectly notes the sharpness of these

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[*] An example of a very rapid change may be seen on Plate VIII. at 12,23 P.M,

internal changes. Since the measured interval between two electric contacts is the datum for computing the velocity, an instantaneous stoppage, such as I accidentally saw, will appear on the record simply as a slowing of the wind, and such very significant facts as that just noted will be necessarily slurred over, even by the most sensitive apparatus of this kind.

However, the more frequent the contacts the more nearly an exact record of the fluctuations may be measured ; and I have, as I have stated, provided that they should be made at every half revolution of the anemometer, that is, as a rule, several times a second *.

I now invite the reader's attention to the actual records of rapid changes that take place in the wind's velocity, selecting as an illustration the first $5\frac{1}{2}$ minutes of the diagram plotted on Plate VII.

The heavy line through points A, B, and C represents the ordinary record of the wind's velocity as obtained from a standard Weather Bureau anemometer during the observations recording the passage of two miles of wind. The velocity, which was, at the beginning of the interval considered, nearly 23 miles an hour, fell during the course of the first mile to a little over 20 miles an hour. This is the ordinary anemometric record of the wind at such elevations as this (47 metres) above the earth's surface, where it is free from the immediate vicinity of disturbing irregularities, and where it is popularly supposed to move with occasional variation in direction, as the weather-cock indeed indicates, but with such nearly uniform movement that its rate of advance is, during any such brief time as two or three minutes, under ordinary circumstances, approximately uniform. This, then, may be called the "wind;" that is, the conventional " wind " of treatises upon aerodynamics, where its aspect as a practically continuous flow is

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* Here we may note the error of the common assumption that the ordinary anemometer, however heavy, will, if frictionless, correctly measure the velocity of the wind, for the existence of " vis inertiæ " it is now seen, is not indifferent, but plays a most important part where the velocity suffers such great and frequent changes as we here see it does, and where the rate at which this inertia is overcome, and this velocity changed, is plainly a function of the density of the fluid, which density we also see reason to suppose itself varies incessantly, and with great rapidity. Though it is probable that no form of barometer in use does justice to the degree of change of this density, owing to this rapidity, we cannot, nevertheless, suppose it to exceed certain limits, and we may treat the present records, made with an anemometer of such exceptional lightness, as being comparatively unaffected by these changes in density, though they exist.

alone considered. When, however, we turn to the record made with the specially light anemometer, at every second, of this same wind, we find an entirely different state of things. The wind, starting with the velocity of 23 miles an hour, at $12^h 10^m 18^s$ rose within 10 seconds to a velocity of 33 miles an hour, and within 10 seconds more fell to its initial speed. It then arose within 30 seconds to a velocity of 36 miles an hour, and so on, with alternate risings and fallings, at one time actually stopping ; and, as the reader may easily observe, passing through 18 notable maxima and as many notable minima, the average interval from a maximum to a minimum being a little over 10 seconds, and the average change of velocity in this time being about 10 miles an hour. In the lower left-hand corner of Plate VII. is given a conventional representation of these fluctuations in which this average period and amplitude is used as a type. The above are facts, the counterpart of which may be noted by any one adopting the means the writer has employed. It is hardly necessary to observe, that almost innumerable minor maxima and minima presented themselves, which the drawing cannot depict.

In order to ensure clearness of perception, the reader will bear in mind that the diagram does not represent the velocities which obtained coincidently, along the length of two miles of wind represented, nor the changes in velocity experienced by a single moving particle during the interval, but that it is a picture of the velocities which were in this wind at the successive instants of its passing the fixed anemometer ; which velocities, indeed, were probably nearly the same for a few seconds before and after registry, but which incessantly passed into, and were replaced by, others, in a continuous flow of change. But although the observations do not show the actual changes of velocity which any given particle experiences in any assigned interval, these fluctuations cannot be materially different in character from those which are observed at a fixed point, and are shown in the diagram. It may, perhaps, still further aid us in fixing our ideas, to consider two material particles as starting at the same time over this two-mile course : the one moving with the uniform velocity of 22·6 miles an hour (33 feet per second), which is the average velocity of the wind as observed for the interval between $12^h 10^m 18^s$ and $12^h 15^m 45^s$ on February 4 ; the other, during the same interval, having the continuously changing velocities actually indicated by the light anemometer, as shown on Plate VII. Their positions at any time may, if desired, be conveniently represented in a diagram where the abscissa of

any point represents the elapsed time in seconds, and the ordinates show the distance, in feet, of the material particle from the starting-point. The path of the first particle will thus be represented by a straight line, while the path of the second particle will be an irregularly curved line, at one time above, and at another time below the mean straight line just described, but terminating in coincidence with it at the end of the interval. If, now, all the particles in two miles of wind were simultaneously accelerated and retarded in the same way as this second particle, that is, if the wind were an inelastic fluid and moved like a solid cylinder, the velocities recorded by the anemometer would be identical with those that obtained along the whole region specified. But the actual circumstance must evidently be far different from this, since the air is an elastic and nearly perfect fluid, subject to condensation and rarefaction. Hence the successive velocities of any given particle (which are in reality the resultant of incessant changes in all directions) must be conceived as evanescent, taking on something like the sequence recorded by these curves a very brief time before this air reached the anemometer, and losing it as soon after.

It has not been my purpose in this paper to enter upon any inquiry as to the cause of this non-homogeneity of the wind. The irregularities of the surface topography (including buildings and every other surface obstruction) are commonly adduced as a sufficient explanation of the chief irregularities of the surface wind ; yet I believe that at a considerable distance above the earth's surface (*e. g.* one mile) the wind may not even be approximately homogeneous, nor have an even flow ; for while, if we consider air as an absolutely elastic and frictionless fluid, any motion impressed upon it would be preserved for ever, and the actual irregularities of the wind would be the results of changes made at any past time, however remote ; so long as we admit that the wind, without being absolutely elastic and frictionless, is nearly so, it seems to me that we may consider that the incessant alternations, which it here appears make the " wind," are due to past impulses and changes which are preserved in it, and which die away with very considerable slowness. If this be the case, it is less difficult to see how even in the upper air, and at every altitude, we might expect to find local variations, or pulsations, not unlike those which we certainly observe at minor altitudes above the ground [*].

* In this connexion, reference may be made to the notable investigations of Helmholtz on Atmospheric movements, *Sitzungsberichte*, Berlin, 1888 –1889.

PART III.—*Application.*

Of these irregular movements of the wind, which take place up, down, and on every side, and are accompanied of necessity by equally complex condensations and expansions, it will be observed that only a small portion, namely, those which occur in a narrow current whose direction is horizontal and sensibly linear, and whose width is only the diameter of the anemometer, can be noted by the instruments I have here described, and whose records alone are represented in the diagram. However complex the movement may appear as shown by the diagram, it is then far less so than the reality, and it is probable, indeed, that anything like a fairly complete graphical presentation of the case in impossible.

I think that on considering these striking curves (Plates V., VI., VII., VIII., and IX.), we shall not find it difficult to admit, at least as an abstract conception, that there is no necessary violation of the principle of the conservation of energy implied in the admission that a body wholly immersed in, and moving with such a wind, may derive from it a force which may be utilized in *lifting* the body, in a way in which a body immersed in the "wind" of our ordinary conception could not be lifted, and if we admit that the body may be lifted, it follows obviously that it may descend under the action of gravity from the elevated position, on a sloping path, to some distance in a direction opposed to that of the wind which lifted it, though it is not obvious what this distance is.

We may admit all this, because we now see (I repeat) that the apparent violation of law arises from a tacit assumption which we, in common with all others, may have made, that the wind is an approximately homogeneously moving body, because moving as a whole in one direction. It is, on the contrary, *always* as we see here, filled (even if we consider only movements in some one horizontal plane) with amazingly complex motions, some of which, if not in direct opposition to the main movement, are relatively so, that is are slower, while others are faster than this main movement, so that a portion is always opposed to it.

From this, then, we may now at least see that it is plainly within the capacity of an intelligence like that suggested by Maxwell, and which Lord Kelvin has called the " Sorting Demon," to pick out from the internal motions those whose direction is opposed to the main current, and to omit those which are not so, and thus, *without the expenditure of energy,* to construct a force which will act against the main current itself.

But we may go materially further, and not only admit that it is not necessary to invoke here, as Maxwell has done in the case of thermodynamics, a being having power and rapidity of action far above ours, but that, in actual fact, a being of a lower order than ourselves, guided only by instinct, may so utilize these internal motions.

We might not, indeed, have conceived this possible, were it not that nature has already, to a large extent, exhibited it before our eyes in the soaring bird*, which sustains itself endlessly in the air with nearly motionless wings, for without this evidence of the possibility of an action which now ceases to approach the inconceivable, we are not likely, even if admitting its theoretical possibility, to have thought the mechanical solution of this problem possible.

But although to show how this physical miracle of nature is to be imitated, completely and in detail, may be found to transcend any power of analysis, I hope to show that this may be possible without invoking the asserted power of " aspiration " relative to curved surfaces, or the trend of upward currents, and even to indicate the probability that the mechanical solution of this problem may not be beyond human skill.

To this conclusion we are invited by the following consideration, among others.

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* " When the condors in a flock are wheeling round and round any spot, their flight is beautiful. Except when rising from the ground, I do not recollect ever having seen one of these birds flap its wings. Near Lima I watched several for nearly half an hour without once taking off my eyes. They moved in large curves sweeping in circles, descending and ascending without once flapping. As they glided close over my head, I intently watched, from an oblique position, the outlines of the separate and terminal feathers of the wing; and if there had been the least vibratory movement these would have blended together, but they were seen distinct against the blue sky. The head and neck were moved frequently and apparently with force, and it appeared as if the extended wings formed the fulcrum on which the movements of the neck, body, and tail acted. If the bird wished to descend, the wings for a moment collapsed; and then, when again expanded, with an altered inclination, the momentum gained by the rapid descent seemed to urge the bird upwards, with the even and steady movement of a paper kite. In the case of any bird *soaring*, its motion must be sufficiently rapid so that the action of the inclined surface of its body on the atmosphere may counterbalance its gravity. The force to keep up the momentum of a body moving in a horizontal plane in that fluid (in which there is so little friction) cannot be great, and this force is all that is wanted. The movement of the neck and body of the condor, we must suppose, is sufficient for this. However this may be, it is truly wonderful and beautiful to see so great a bird, hour after hour, without any apparent exertion, wheeling and gliding over mountain and river."—Darwin's Journal of the Various Countries Visited by H.M.S. ' Beagle,' pp. 223–224.

We will presently examine the means of utilizing this potentiality of internal work in order to cause an inert body wholly unrestricted in its motion and wholly immersed in the current, to *rise*; but first let us consider such a body (a plane) whose movement is restricted in a horizontal direction, but which is free to move between frictionless vertical guides. Let it be inclined upward at a small angle towards a horizontal wind, so that only the vertical component of the pressure of the wind on the plane will affect its motion. If the velocity of the wind be sufficient, the vertical component of pressure will equal or exceed the weight of the plane, and in the latter case the plane will rise indefinitely.

Thus, to take a concrete example, if the plane be a rectangle whose length is six times its width, having an area of 2·3 square feet to the pound, and be inclined at an angle of 7°, and if the wind have a velocity of 36 feet per second, experiment shows that the upward pressure will exceed the weight of the plane, and the plane will rise, if between vertical nearly frictionless guides, at an increasing rate, until it has a velocity of 2·52 feet per second *, at which speed the weight and upward pressure are in equilibrium. Hence there are no unbalanced forces acting, and the plane will have attained a state of uniform motion.

For a wind that blows during 10 seconds, the plane will therefore rise about 25 feet. At the beginning of the motion, the inertia of the plane makes the rate of rise less than the uniform rate, but at the end of 10 seconds the inertia will cause the plane to ascend a short distance after the wind has ceased, so that the deficit at the beginning will be counterbalanced by the excess at the end of the assigned interval.

We have just been speaking of a material heavy plane permanently sustained in vertical guides, which are essential to its continuous ascent in a uniform wind, but such a plane will be lifted and sustained *momentarily* even if there be no vertical guides, or, in the case of a kite, even if there be no cord to retain it, the inertia of the body supplying for a brief period the office of the guides or of the cord. If suitably disposed, it will, as the writer has elsewhere shown, under the resistance to the horizontal wind, imposed only by its inertia, commence to move, not in the direction of the wind, but nearly vertically. Presently however, as we recognize, this inertia must be overcome, and as the inclined plane takes up more and more the motion of the wind, the lifting effect must grow less and less (that is to say, if the wind

* See " Experiments in Aerodynamics," by S. P. Langley, 'Smithsonian Contribution to Knowledge,' 1891.

be the approximately homogeneous current it is commonly treated as being), and finally ceasing altogether, the plane must ultimately fall. If, however, a counter-current is supposed to meet this inclined plane, before the effect of its inertia is exhausted, and consequently before it ceases to rise, we have only to suppose the plane to be rotated through 180° about a vertical axis, without any other call for the expenditure of energy, to see that it will now be lifted still higher, owing to the fact that its inertia now reappears as an active factor. The annexed sketch (fig. 1) shows a typical representation of what might be supposed to happen with a model inclined plane freely suspended in the air, and endowed with the power

Fig.1.

of rotating about a vertical axis so as to change the aspect of its constant inclination, which need involve no (theoretical) expenditure of energy, even although the plane possess inertia. We see that this plate would rise indefinitely by the action of the wind in alternate *directions*.
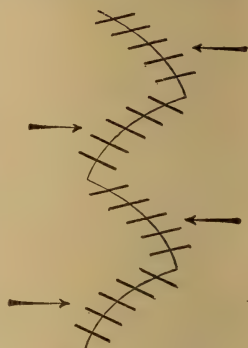
The disposition of the wind which is here supposed to cause the plane to rise appears at first sight an impossible one, but we shall next make the important observation that it becomes virtually possible by a method which we shall now point out, and which leads to a practicable one which we may actually employ.

Figure 2 shows the wind blowing in one constant direction, but alternately at two widely varying velocities, or rather (in the extreme case supposed in illustration) where one of the velocities is negligibly small, and where successive pulsations in the same direction are separated by intervals of calm.

A frequent alternation of velocities, united with constancy of absolute direction, has previously been shown here to be the ordinary condition of the wind's motion ; but attention is now particularly called to the fact that while these unequal velocities may be in the same direction as regards the surface of the earth, yet as regards the *mean* motion of the wind they are in opposite directions, and will produce on a plane, whose inertia enables it to sustain a sensibly uniform motion with the mean velocity of this variable wind, the same lifting effect as if these same alternating winds were in absolutely opposed directions, provided that the constant inclination of

the plane alternates in its aspect to correspond with the changes in the wind.

It may aid in clearness of conception, if we imagine a set of fixed coordinates X Y Z passing through O, and a set of movable coordinates *x y z,* moving with the velocity and the direction of the mean wind. If the moving body is referred to these first only, it is evidently subject to pulsations which take place in the same directions on the axis of X, but it must be also evident that if referred to the second or movable coordinates, these same pulsations may be, and are, in opposite directions. This, then, is the case we have just considered, and if we suppose the plane to change the aspect * of its (constant) inclination as the direction of the pulsations changes, it is evident that there must be a gain in altitude with every pulsation, while the

Fig. 2.

plane advances horizontally with the velocity of the mean wind.
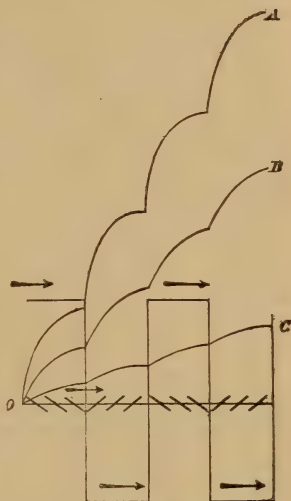
During the period of maximum wind velocity, when the wind is moving faster than the plane, the rear edge of the latter must be elevated. During the period of minimum velocity, when the plane, owing to its inertia, is moving faster than the wind, the front edge of the plane must be elevated. Thus the vertical component of the wind pressure, as it strikes the oblique plane, tends in both cases to give it a vertical upward thrust. So long as this thrust is in excess of the weight to be lifted, the plane will rise. The rate of rise will be greatest at the beginning of each period, when the relative velocity is greatest, and will diminish as the resistance produces " drift;" *i. e.* diminishes relative velocity. The curved line O B in the vignette represents a typical path of the plane under these conditions.

It follows from the diagram (fig. 1) that, other things being equal, the more frequent the wind's pulsations, the greater will be the rise of the plane; for since during each period of

* We do not for the moment consider how this change of aspect is to be mechanically effected ; we only at present call attention to the fact that it involves, in theory, no expenditure of energy.

steady wind the rate of rise diminishes, the more rapid the pulsations, the nearer the mean rate of rise will be to the initial rate. The requisite frequency of pulsations is also related to the inertia of the plane, as the less the inertia, the more frequent must be the pulsations in order that the plane shall not lose its relative velocity.

It is obvious that there is a limit or weight which cannot be exceeded, if the body is to be sustained by any such fluctuations of velocity as can be actually experienced. Above this limit of weight the body will sink. Below this limit the lighter the body is the higher it will be carried, but with increasing variability of speed. That body, then, which has the greatest weight per unit of surface will soar with the greatest steadiness, if it soar at all, not on account of this weight *per se*, but because the weight is an index of its inertia.

The reader who will compare the results of experiments made with any artificial flying models, like those of Penaud, with the weights of the soaring birds as given in the tables by M. Mouillard, or other authentic sources, cannot fail to be struck with the great weight in proportion to wing-surface which nature has given to the soaring bird, compared with any which man has yet been able to imitate in his models.

This fact of the weight of the soaring bird in proportion to its area has been again and again noted, and it has been frequently remarked that without weight the bird could not soar, by writers who felt that they could very safely make such a paradoxical statement, in view of the evidence nature everywhere gave that this weight was indeed in some way necessary to rising. But these writers have not shown, so far as I remember, how this necessity arises, and this is what I now endeavour to point out[*].

It has not here been shown what limit of weight is imposed to the power of an ordinary wind to elevate and sustain, but it seems to me, and I hope that it may seem to the reader, that the evidence that there is *some* weight which the action of the wind is sufficient to permanently sustain under these conditions in a free body, has a demonstrative character, although no quantitative formula is offered at this stage of the investigation. It is obvious that, if this weight is sus-

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[*] It is perhaps not superfluous to recall here that, according to the researches of Rankine, Froude, and others, a body moulded in wave-line curves would, if frictionless, continue to move indefinitely against an opposed wind, in virtue of inertia and once acquired velocity, and also to recall how very small the effect of fluid friction in the air has been shown to be (by the writer in a previous investigation).

tainable at any height, gravity may be utilized to cause the body (which we suppose to be a material plane) to descend on an inclined course, to some distance, even against the wind.

I desire, in this connexion, to remark that the preceding experiments and deductions, showing that a material free plane *, possessing sufficient inertia, may in theory rise indefinitely by the action of an ordinary wind, without the expenditure of work from any internal source (as well as those statements which follow), when these explanations are once made, have a character of obviousness, which is due to the simplicity of the enunciation, but not, I think, to the familiarity of the explanation, for though attention is beginning to be paid by meteorologists to the rapidity of these wind fluctuations, I am not aware that their effects have been so exhibited, or, especially, that they have been presented in this connexion, or that the conclusions which follow have been drawn from them.

We have here seen, then, how pulsations of sufficient amplitude and frequency, of the kind which present themselves in nature, may, in theory, furnish energy not only sufficient to sustain, but actually to elevate, a heavy body moving in and with the wind at its mean rate.

It is easy now to pass to the practical case which has been already referred to, and which is exemplified in nature, namely, that in which the body (*e. g.* the bird soaring on rigid wings, but having power to change its inclination) uses the elevation thus gained to move against the wind, without expending any sensible amount of its own energy. Here the upward motion is designedly arrested at any convenient stage, *e. g.* at each alternate pulsation of the wind, and the height attained is utilized so that the action of gravity may carry the body by its descent in a curvilinear path (if necessary) against the wind. It has just been pointed out that if some height has been attained, the theoretical possibility of *some* advance against the wind in so falling hardly needs demonstration, though it may not unnaturally be supposed that the relative advance so gained must be insignificant, compared with the distance travelled by the mean wind while

* I use the word " plane," but include in the statement all suitable modifications of a curved surface.

I desire to recall attention to the paragraph in " Experiments in Aerodynamics," in which I caution the reader against supposing that by investigating plane surfaces I imply that they are the best form of surface for flight; and I repeat here that, as a matter of fact, I do not believe them to be so. I have selected the plane simply as the best form for preliminary experiment.

the body was being elevated, so that on the whole the body is carried by the wind farther than it advances against it.

This, however, probably need not be in fact the case, there being, as it appears to me from experiment and from deduction, every reason to believe that under suitable conditions the advance may be greater than the recession, or that the body falling under the action of gravity along a suitable path may return against the wind, not only from Z to O, the point of departure, but farther, as is here shown.

I repeat, however, that I am not at the moment undertaking to demonstrate how the action is mechanically realizable in actual practice, but only that it is possible. It is for this purpose, and to understand more exactly that it can be effected, not only by the process indicated in the second illustration (fig. 2) but by another and probably more useful one (and nature has still others at command), that I have considered another treatment of the same conditions, of wind-pulsations always moving in the same horizontal direction, but for brief periods, interrupted by equal intervals of calm. In this third illustration (fig. 3) we suppose the body to use the height gained in each pulsation, to enable it to descend after each such pulsation and advance against the direction of the wind.
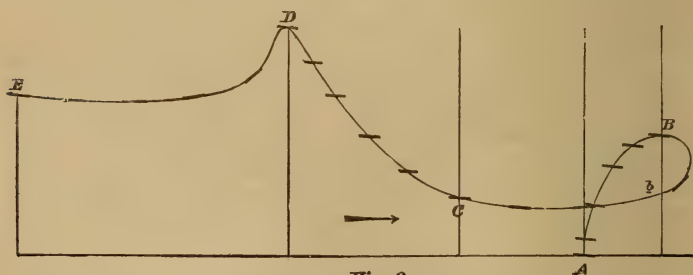
Fig. 3.

The portion AB of the curve represents the path of the plane surface from a state of rest at A, where it has a small upward inclination toward the wind. If a horizontal wind blow upon it in the direction of the arrow, the first movement of the plane will not be in the direction of the wind, but, as is abundantly demonstrated by the writer in " Experiments in Aerodynamics," it will rise in a nearly vertical direction, if the angle be small. The wind, continuing to blow in the same direction, at the end of a certain time, the plane, which has risen (owing to its inertia, and in spite of its weight) to the successive positions shown, is taking up more and more of the

horizontal velocity of the wind, and consequently opposing less resistance to it, and therefore moving more and more laterally, and rising less and less, at every successive instant.

If the wind continued indefinitely, the plane would ultimately take up its velocity, and finally, of course, fall, when this inertia ceased to oppose resistance to the wind's advance. I have supposed, however, the wind pulsation to cease at the end of a certain brief period, and, to fix our ideas, let us suppose this period to be five seconds. At this moment the period of calm begins, and now let the plane, which is supposed to have reached the point B, change its inclination about a horizontal axis to that shown in the diagram, falling at first nearly vertically, with its edge on the line of its descent, so as to acquire speed, and this speed acquired, by constantly changing its angle, glide down the curve B*b*C, so that the plane shall be tangential to it at every point of its descending advance. At the end of five seconds of calm it has reached the position C, near the lowest point of its descent, which there is no contradiction to known mechanical laws in supposing *may* be higher than A, and which in fact, according to the most accurate data the writer can gather, *is* higher, in the case of the above period, and in the case of such an actual plane as has been experimented upon by him.

Now, having reached C, at the end of the five seconds' calm, if the wind blow in the same direction and velocity as before, it will again elevate the plane on the latter's presenting the proper angle, but this time under more favourable circumstances, for at this time the plane is already in motion in a direction opposed to that of the wind, and is already higher than it was in its original position A. Its course, therefore, will be nearly that along the curve CD, during all which time it maintains the original angle *a* or one very slightly less. Arrived at D, and at the instant when the calm begins, it falls, with varying inclination, to the lowest position E (which may be higher than C), which it attains at the end of the five seconds of calm, then rises again (still nearly at the angle *a*) to a higher position, and so on ; the alternation of directions of motion, at the end of each pulsation, growing less and less sharp, and the path finally taking the character of a sinuous curve. We have here assumed that the plane goes against the wind and rises at the same time, in order to illustrate that this is possible, though either alternative may be employed, and the plane, in theory at least, may maintain on the whole a rapid and nearly horizontal, or a slow and nearly vertical course, or anything between.

It is not meant, either, that the alternations which would be

observed in nature are as sharp as those here represented, which are intentionally exaggerated, while in all which has just preceded, by an equally intentional exaggeration of the normal action, the wind-pulsations have been supposed to alternate with absolute calm. This being understood, it is scarcely necessary to point out that if the calm is not absolute, but if there are simply frequent successive winds or pulsations of wind of considerably differing velocity (such as the anemometer observations show are realized in nature), the same general effect will obtain*, though we are not entitled to assume from any demonstration thus far given that the total advance will be necessarily greater than that of the whole distance the mean wind has travelled. It may also be observed that the actual actions of the soaring bird may be, and doubtless are, more complex in detail than those of this diagram, while yet in their entirety depending on the principles it sets forth.

The theoretical possibility at least will now, it is hoped, be granted, not only of the body's rising indefinitely, or of its descending in the interval of calm to a higher level C than it rose from at A, but of its advancing against the calm or light wind through a distance BC, greater than that of AB, and so on. The writer, however, repeats that he has reason to suppose, from the data obtained by him, that this is not only a theoretical possibility, but a mechanical probability under the conditions stated, although he does not here offer a quantitative demonstration of the fact, other than by pointing to the movements of the soaring bird and inviting their reconsideration in the light of the preceding statements.

The bird, by some tactile sensibility to the pressure and direction of the air, is able, in nautical phrase, to " see the wind " † and to time its movements so that, without any reference to its height from the ground, it reaches the lowest portion of its descent near the end of the more rapid wind-pulsation ; but the writer believes that to cause these adaptive

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* The rotation of the body about a vertical axis so as to change the aspect of the inclination, as in the first figure, may be illustrated by the well-known habit of many soaring birds, of moving in small closed curves or spirals, but it may also be observed, in view of the fact that even in intervals of relative calm during which the body descends, there is always some wind,—that in making the descents, if the body, animate or inanimate, maintain its direct advance, this wind tends to strike on the upper side of the plane or pinion. Mr. G. E. Curtis offers the suggestion that the soaring bird avoids such a position when possible, and therefore turns at right angles to, or with, the wind, and that this may be an additional reason for its well-known habit of moving in spirals.

† Mouillard.

changes in an otherwise inert body, with what might almost be called instinctive readiness and rapidity, does not really demand intelligence or even instinct, but that the future aerodrome may be furnished with a substitute for instinct, in what may perhaps allowably be called a mechanical brain, which yet need not, in his opinion, be intricate in its character. His reasons for this statement, which is not made lightly, must, however, be reserved for another time.

It is hardly necessary to point out that the nearly inert body in question may also be a human body, guided both by instinct and intelligence, and that there may thus be a sense in which human flight may be possible, although flight depending wholly upon the action of human muscles be for ever impossible.

Let me resume the leading points of the present memoir in the statement that it has been shown :—

(1) That the wind is not even an approximately uniform moving mass of air, but consists of a succession of very brief pulsations of varying amplitude, and that, relatively to the mean movement of the wind, these are of varying direction.

(2) That it is pointed out that hence there is a potentiality of " internal work " in the wind, and probably of a very great amount.

(3) That it involves no contradiction of known principles to declare that an inclined plane, or suitably curved surface, heavier than the air, freely immersed in, and moving with the velocity of the mean wind, can, if the wind-pulsations here described are of sufficient amplitude and frequency, be sustained or even raised indefinitely without expenditure of internal energy, other than that which is involved in changing the aspect of its inclination at each pulsation.

(4) That since (A) such a surface, having also power to change its inclination, *must* gain energy through falling during the slower, and expend energy by rising during the higher, velocities ; and that (B) since it has been shown that there is no contradiction of known mechanical laws in assuming that the surface *may* be sustained or *may* continue to rise indefinitely, the mechanical possibility of some advance against the direction of the wind follows immediately from this capacity of rising. It is further seen that it is at least possible that this advance against the wind may not only be attained relatively to the position of a body moving with the speed of the mean wind, but absolutely, and with reference to a fixed point in space.

(5) The statement is made that this is not only mechanically possible, but that, in the writer's opinion, it is realizable in practice.

Finally, these observations and deductions have, it seems to me, an important practical application not only as regards a living creature like the soaring bird but still more as regards a mechanically constructed body, whose specific gravity may probably be many hundred or even many thousand times that of the atmosphere. We may suppose such a body to be supplied with fuel and engines, which would be indispensable to sustain it in a calm, and yet which we now see might be ordinarily left entirely inactive, so that the body could supposably remain in the air and even maintain its motion in any direction without expending its energy, except as regards the act of changing the inclination or aspect which it presents to the wind, while the wind blew.

The final application of these principles to the art of aerodromics seems then to be, that while it is not likely that the perfected aerodrome will ever be able to dispense altogether with the ability to rely at intervals on some internal source of power, it will not be indispensable that this aerodrome of the future shall, in order to go any distance—even to circumnavigate the globe without alighting,—need to carry a weight of fuel which would enable it to perform this journey under conditions analogous to those of a steamship, but that the fuel and weight need only be such as to enable it to take care of itself in exceptional moments of calm.

Smithsonian Institution,
Washington, D. C., August 1893.

XLII. *A new Electrical Theorem.*
By Thomas H. Blakesley, *M.A.*[*]

THE very short paper which I shall read to the Society contains the account of a Theorem which, though admitting of easy proof, appears, so far as my inquiries have gone, to have hitherto escaped notice.

In order to state the matter briefly, it will be well to adopt the following definition :—

If in any system of conductors, however reticulated, two or more modes of disposition of sources of electromotive force produce in every part of the network the same current, such systems of disposition are called *equivalent systems*. Then the theorem is as follows :—In any system of conductors, possessing seats of electromotive force at any number of points, if any of these sources be supposed to move continuously along the various bars of the conducting system,

and, where a point of junction is encountered, each to become a seat of the *same* electromotive force in *each* of the newly encountered bars (of course leaving the resistance of the source behind), then the disposition at any moment is equivalent to that at any other moment, and therefore to the original disposition. [Of course the direction of the electromotive force must be carefully maintained the same : if it is towards the knot before crossing it, it must be away from the knot after passing it.] The proof need only refer to the passing of a knot point, for no one will doubt that if the sources only move in an *unbranching* portion of the conductor the currents in different parts of the system will remain the same.
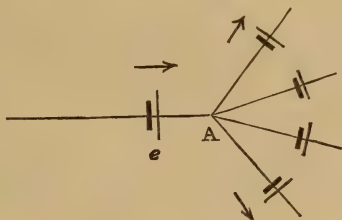
Let therefore the source *e* approach the point A at which its path splits into *n* other ways. In each of the *n* bars suppose a source *e* inserted as directed, then these *n* alone must be equivalent to the single source before reaching A ; for if the *n* sources are reversed, the current due to these sources in every portion of the system is reduced to zero. The reversed *n* sources would therefore alone produce currents in the system equal numerically, but opposite in direction, to those produced by the single source. Hence it follows that the *n* sources (not reversed) will produce the same current as the single source.

The principle of the superposition of currents enables us to apply this result to each source of the system, and therefore to prove the truth of the theorem in its complete generality.

In equivalent systems, since the current in every part remains the same, the total power expended remains the same ; and equivalent systems might have been defined as those which produce the same expenditure of power in each part ; and therefore the total power of the sources remains the same.

From the point of view of Kirchhoff's theorem $\Sigma e = \Sigma \cdot rc$ for any closed path in a network, the above general theorem may seem to some minds even plainer and more easily proved than on the method of demonstration which I have employed.

For it is plain from the method of derivation, that if a seat of electromotive force exists in any closed Kirchhoff path it can never leave it ; and if in the movement of the sources one of them approaches the closed path under consideration, at the encounter it becomes in that path two equal sources acting in opposite directions.

If, therefore, Σe remains the same for any path and r remains the same for every part, then obviously c must remain the same for any portion of that path, and therefore for every part of the network.

The following propositions flow immediately from the main proposition :—

(1) If a closed continuous surface contains any region of any network, and some bar which cuts the surface contains, or by derivation as above can be made to contain, the seat of an electromotive force, then that source can be done away with without disturbing the currents in any portion of the system provided that in the other bars which cut the surface sources of electromotive force be inserted of equal value but of opposite direction as regards inside and outside of the surface ; for it is clear that such sources would result from the migration of sources in one direction.

(2) If two systems of electromotive forces are equivalent, one may be derived from the other. For if system A is equivalent to system B, and we suppose $\frac{A}{2}$ to represent a distribution identical with A as regards positions, but of half the electromotive force in any case, then $\frac{A}{2} + \frac{B}{2}$ is equivalent to A or B alone. Now if any Kirchhoff path containing a source from $\frac{A}{2}$ does not also contain a source from $\frac{B}{2}$, then Kirchhoff's law would be outraged ; for the sum of the electromotive forces in that path would be only half what they are from A alone, whereas the currents and resistances remain the same. Hence for every Kirchhoff path there must be equal sources from each system. Either system may now have its elements moved up to those of the other system ; any resulting side branchings will be the same (though differing in sign) whether derived from $\frac{A}{2}$ or from $\frac{B}{2}$, and must necessarily produce no effect by themselves, because if we consider $\frac{B}{2}$ to be reversed, the whole effect of $\frac{A}{2}$ and $\frac{B}{2}$, *now in the same bars*, will be zero.

XLIII. *The Viscosity of Liquids.*
By Owen Glynne Jones, *B.Sc.*[*]

THE object of this paper is to point out a method for the accurate determination of the viscosity of highly viscous liquids. The author would prefer to delay the publication of most of his results till the experiments are completed. The advantages and disadvantages of the method, and its applicability to the determination of viscosities such as those of alcohol and water, are not yet entirely ascertained, but such of these points as have already suggested themselves will be noticed at the end of the paper.

Sir G. Stokes has long since shown that if a sphere moves vertically in an infinite liquid under the action of gravity only, it in course of time assumes a constant speed :

$$V = \frac{2}{9} g a^2 \frac{(\sigma - \rho)}{\mu},$$

where a is the radius of the sphere, σ its density, ρ that of the liquid in which it moves, and μ the viscosity of the liquid. The equation assumes that there is no slipping at the surface of the sphere, *i. e.*, that the coefficient of sliding-friction is infinite. The effect of such sliding-friction would be to modify the equation thus :

$$V = \frac{2}{9} g a^2 \frac{\sigma - \rho}{\mu} \frac{\beta a + 3\mu}{\beta a + 2\mu},$$

where β is the coefficient of sliding-friction.

The method employed by the author consists in the measurement of the downward speed of a sphere of mercury through the viscous liquid. The amount of mercury used is taken sufficiently small to render possible the measurement, correct to ·1 per cent., of the time taken to pass through a distance of about 25 centim. This also renders legitimate the assumptions that the mercury remains spherical during its motion, and that the liquid in an ordinary burette about 1·5 centim. internal diameter is for purposes of calculation of infinite extent, the motion of such a sphere falling down the burette along its centre line being unaffected by the sides of the vessel.

The burette is jacketed with water kept as nearly as possible at constant temperature. The temperature of water direct from the main was observed last autumn to vary to an

extent of only $\cdot 03°$ C. in an hour and a half, and good results were then obtained for the viscosity of glycerine. Within the last fortnight the main temperature has not been nearly so constant, and more has been learnt concerning the variation of viscosity with temperature than the absolute value of viscosity for any definite liquid.

The mass of a sphere of mercury suitable for glycerine would be between $\cdot 003$ and $\cdot 010$ grm. This is too small to be determined with sufficient accuracy by direct weighing, with a balance estimating to one tenth of a milligramme. But there is no necessity to determine such a mass directly.

Let a mass of mercury weighing about $\cdot 1$ grm. be taken and weighed carefully. Let it be divided into about 12 parts, approximately equal to each other. Let the speed of each through a column of very viscous liquid, such as glycerine or clear castor-oil, be determined. Then, using Stokes's result,

$$\mu \propto \frac{a^2}{v},$$

$$\therefore \quad \mu \propto \frac{m^{\frac{2}{3}}}{v} \; ;$$

and for a given liquid with constant viscosity

$$m \propto v^{\frac{3}{2}},$$

or
$$m = k v^{\frac{3}{2}}.$$

Hence
$$\Sigma m = k \Sigma v^{\frac{3}{2}}.$$

But $\Sigma m = \mathrm{M}$, the whole mass of mercury, and $\Sigma v^{\frac{3}{2}} = \mathrm{V}^{\frac{3}{2}}$, the speed that the whole mass would have if it fell as a sphere through the infinite liquid. Perhaps taken as a whole the mercury would not fall as a sphere, and the liquid in the burette would not be as of infinite extent; but by this subdivision such errors are avoided.

We thus get the speed V corresponding to the mass M, and these values can be applied at once in the equation

$$\mu = \frac{2}{9} g a^2 \frac{(\sigma - \rho)}{\mathrm{V}},$$

or
$$= \frac{2}{9} g \left(\frac{3\mathrm{M}}{4\pi\sigma} \right)^{\frac{2}{3}} \frac{\sigma - \rho}{\mathrm{V}} ;$$

for
$$\mathrm{M} = \frac{4}{3} \pi a^3 \sigma, \quad \text{and} \quad a^2 = \pi \left(\frac{3\mathrm{M}}{4\pi\sigma} \right)^{\frac{2}{3}}.$$

Moreover the mass of each of the smaller spheres may be easily estimated, since

$$\frac{m}{M} = \left(\frac{v}{V}\right)^{\frac{3}{2}},$$

and

$$m = \left(\frac{v}{V}\right)^{\frac{3}{2}} M.$$

The author has been able in this way to determine the mass of a small sphere (and hence its radius) weighing about ·003 grm., correct to four significant figures. Having thus determined its dimensions, it may be employed for other liquids than that by which these dimensions were obtained.

But the important question suggests itself whether μ is simply inversely proportional to the speed of the falling sphere, or whether, as some maintain, there is a finite coefficient of sliding-friction, and a definite amount of slipping at the surface, which will render the connexion between v and m much more complicated.

This may be tested in a simple manner by observing the speed V for a small mass, dividing it into two parts, and observing the speeds v_1 and v_2 for each part in the same viscous liquid at the same temperature. If there be no sliding-friction,

$$V^{\frac{3}{2}} = v_1^{\frac{3}{2}} + v_2^{\frac{3}{2}}.$$

If sliding-friction exists the effect will be to render the V calculated in the above equation from v_1 and v_2 greater than the observed speed for the undivided mass, the divergence being most clearly shown when the two parts are as nearly as possible equal to each other.

For let us assume that the whole is divided into two equal parts, and that the two speeds observed are V and v_1, corresponding to the two radii A and a.

Now $A^3 = 2a^3$, and A is therefore $= 2^{\frac{1}{3}}a$.

With sliding-friction,

$$V = kA^2 \cdot \frac{\beta A + 3\mu}{\beta A + 2\mu},$$

$$= 2^{\frac{2}{3}}ka^2 \cdot \frac{1·26\beta a + 3\mu}{1·26\beta a + 2\mu},$$

and

$$v = ka^2 \cdot \frac{\beta a + 3\mu}{\beta a + 2\mu},$$

then the speed calculated for the whole mass from the formula

$$V^{\frac{3}{2}} = v_1^{\frac{3}{2}} + v_2^{\frac{3}{2}} = 2v^{\frac{3}{2}}$$

would be

$$V' = 2^{\frac{2}{3}} \cdot ka^2 \cdot \frac{\beta a + 3\mu}{\beta a + 2\mu}.$$

The ratio of $\dfrac{V'}{V}$ is therefore

$$\frac{\beta a + 3\mu}{\beta a + 2\mu} \cdot \frac{1 \cdot 26\beta a + 2\mu}{1 \cdot 26\beta a + 3\mu}.$$

Since all the quantities involved are positive, this ratio is evidently greater than unity. As β varies from ∞ to zero, the value of the ratio increases from 1 to a maximum $1 + k$, and then diminishes to 1 again. Thus the divergence between the calculated and the observed speeds does not become greater as the coefficient of sliding-friction diminishes, although this divergence is actually due to the sliding.

Taking the value ·04 centim. for the radius of the sphere, the maximum value of k will be $\dfrac{1}{44}$, the divergence thus amounting to about $2\frac{1}{2}$ per cent. The ratio $\dfrac{\mu}{\beta}$ that gives this result is $\dfrac{1}{55}$ or $\beta = 55\mu$.

If we assume $\dfrac{\mu\rho}{\beta}$ to have the same value for glycerine that Helmholtz assigns to water, the difference between the observed and the calculated speeds will amount to about 1 in 144 for such spheres ($a = ·04$ centim.) as were employed in the investigation.

Various experiments were recently made by the author to test these results; considerable difficulty was experienced in keeping the temperature constant, except when this was 0° C. The tests hitherto made are not regarded as final, and the author would prefer to defer their publication until the series of experiments is complete. But the divergences from the simple law as at first assumed are in all cases within the limits of experimental error, and the method of determining viscosity is not shown to be defective by those test experiments. The temperature difficulty is not so serious in the case of colza-oil, which is one of the liquids experimented upon. The error involved with speeds not exceeding 2 centim. per second through that liquid did not range beyond $\pm 0·2$ per cent., and it was as usual to get positive errors as to get negative. Times were estimated only to the same degree of accuracy.

It is possible that sliding may occur if the speed of the

sphere M exceeds a certain limiting value. This also is obviated by determining its speed indirectly as $(\Sigma v^{\frac{3}{2}})^{\frac{2}{3}}$, since each individual portion travels so much more slowly.

There is another reason why better results may be expected by this process of subdivision. Mercury is liquid, and a sphere would be deformed if it passed rapidly through the viscous medium. Its speed would be diminished, and it could not be dealt with directly by the fundamental equation connecting μ and V. But by subdivision the masses and speeds dealt with are reduced to such an extent that we may confidently assume the shapes to remain spherical. If the deformation thus produced were appreciable, it could again be manifested by the application of the formula

$$\mathrm{V}^{\frac{3}{2}} = \Sigma (v^{\frac{3}{2}}).$$

The calculated V′ would be greater than the observed V, the error being of the same sign as that produced by the neglect of any possibly existing sliding-friction.

The error produced by the sides of the burette, which may be so near as to retard the downward motion, is also diminished by the subdivision of the original mass. This also would have the same sign as the other errors specified. The simplest way of testing its existence is to insert into the upper portion of the burette-tube a thin glass cylinder of smaller diameter, and to send down a sphere along the axis of these two concentric cylinders. In the upper portion of its path the sphere is at a smaller distance from the boundary of the liquid than in the lower portion. If the sides actually affect the motion, the speed of the sphere will suddenly change when it enters into the wider portion of the liquid column. If the change of speed is not appreciable, it may be assumed that the diameter of the burette is sufficiently large.

It has hitherto been assumed that we have the means of keeping the temperature of the liquid constant. This is of the utmost importance, inasmuch as the temperature-variation of viscosity is rarely inconsiderable. The viscosity of glycerine changes from 45 to 8 in the range of 16° from 4° to 20° C. At a temperature of 15° C. there is a 10-per-cent. variation per degree change. This implies that to get the viscosity correct to four significant figures the thermometers employed should read to ·01° C.

In the case of olive-oil, using Osborne Reynolds's empirical formula for the viscosity at any temperature between 15° and 50° C.,

$$\mu = 3\cdot265 \, e^{-\cdot0123\,t}.$$

Any such equation, $\mu = Ae^{-kt}$, means that the percentage variation per degree is constant, since its differential equation is

$$\frac{d\mu}{\mu \, dt} = \text{constant}.$$

For olive-oil this constant is ·0123 and the percentage variation is 1·23 for any temperature within the given limits—about one ninth of the change in the viscosity of glycerine per degree. In this case the thermometer should read to $\frac{1}{12}$ of a degree. It is useless to calculate the viscosity of glycerine beyond the fourth significant figure unless there be means for the accurate determination of temperature correct to at any rate ·001° C.

The liquids experimented upon are all bad conductors of heat, and though this is advantageous in that the change of temperature during the course of an observation is not likely to be great, it is a disadvantage in that it takes a long time for the temperature to become uniform throughout the length of the column of liquid. It is quite possible for a difference of temperature of ·1° C. to exist at points in the liquid 1 dcm. apart even though the water has been circulating in the jacket for some minutes.

The temperature can only be expected to be uniform when the circulation has been of constant temperature for about 20 minutes.

But it is of importance to note that small variations in the temperature of the liquid at different points along the path of the falling sphere need not trouble us much if the mean temperature be known. And, similarly, small changes in the mean temperature of the whole during the course of an experiment may be harmless if the mean temperature during the interval be known.

For it can be proved that the speed of flow of a body is the speed corresponding to the mean temperature, however the temperature may vary along the length, if the speed be small and if the temperature-variation be small. Both these conditions are satisfied in the actual experiments undertaken. The inertia of the body is so small that it almost instantly assumes the limiting speed corresponding to the temperature of that part of the liquid through which it is moving.

Let the temperature vary from θ_1 at one end to θ_2 at the other end of the column of length l. Let the corresponding viscosities be μ_1 and μ_2; and let θ and μ be the temperature and viscosity at a point at distance x from the top of the column.

For the small change of temperature assumed,

$$\frac{\mu - \mu_1}{\mu_1 - \mu_2} = \frac{\theta - \theta_1}{\theta_1 - \theta_2},$$

or

$$\mu = A(\theta_1 - \theta) + \mu_1.$$

Now, if dt be the time taken to traverse the distance dx, the general equation of steady motion gives us

$$dt = \frac{\mu\, dx}{k}$$

$$= \frac{1}{k} \{\mu_1 + A(\theta_1 - \theta)\}\, dx.$$

Let $\theta = f(x)$, such that

$$\theta_1 = f(0) \quad \text{and} \quad \theta_2 = f(l).$$

Then the time taken for the whole descent

$$T = \frac{1}{k} \int_0^l \{\mu_1 + A(\theta_1 - \theta)\}\, dx$$

$$= \frac{1}{k} \left\{ \mu_1 l + A\theta_1 l - A \int_0^l f(x)\, dx \right\}.$$

But

$$\int_0^l f(x)\, dx = B, \text{ the area of the temperature-curve,}$$

$$= l \,.\, \theta_m, \text{ if } \theta_m \text{ be the mean temperature};$$

$$\therefore \quad T = \frac{1}{k} \{\mu_1 + A(\theta_1 - \theta_m)\} l.$$

But if the temperature had been uniformly θ_m throughout the length l, the time τ would have been

$$\tau = \frac{l}{k} \mu_m,$$

where

$$\mu_m = \mu_1 + A(\theta_1 - \theta_m).$$

Hence

$$T = \tau.$$

It therefore is only necessary to determine the mean temperature during the interval, and even this is unnecessary if our object is to compare two masses of mercury by their speeds, if they are made to follow each other sufficiently rapidly for the mean temperatures to remain constant in the two cases.

If a variation in temperature along the tube be suspected,

the test is simply to send down a minute sphere and observe its speed for short lengths all along the tube. This speed is constant if the temperature is uniform. In accurate estimations of absolute viscosity the variation in speed should not exceed 1 in 1000 along the tube.

It is probably preferable to read the temperature by a thermometer inserted in the viscous liquid, using a burette of sufficient bore to render the insertion safe. But good results have been obtained with the thermometer in the water-jacket, tied close to the inner tube ; this arrangement serves quite well when the water-jacket is fairly constant in temperature.

An observation with glycerine cannot be called good if the temperature-variation exceeds ·03° C., and any that are made with greater variation must be discounted. This conclusion is forced upon one when the periods of falling are taken for the same sphere twenty or thirty times in succession. The curve plotted, connecting the temperature with the time of falling, is a straight line within a range of 1° C., and it is generally found that the points farthest from the straight line correspond to the greatest variation of temperature during the fall. Such a curve supplies us with the means of determining the correction necessary to reduce a speed at one temperature to that at another.

To ensure that the falling sphere shall remain in the axis of the burette, the burette and its jacket are mounted vertically on a stand fitted with levelling-screws, such as that of an ordinary Jolly's balance. The mercury is let down into the burette by a small funnel. The speed is determined by observing the time taken to pass from one mark to another. The distance taken was generally about 50 centim., measured correct to $\frac{1}{2}$ millim., the time taken to traverse that distance being from 100 to 200 seconds. The time was measured with an ordinary watch beating fifths-seconds, or more recently with a Siemens chronograph. In either case the masses of mercury were so chosen that the probable error in a single observation was 1 in 1000.

The following results are for glycerine at temperatures of 18°·28 and 4°·35 C. The former agrees closely with a value obtained by interpolation from Schöttner's results. The latter would appear to be considerably higher than the corresponding interpolation.

A. Mass of mercury taken, ·03737 grm. This was divided
   into 12 parts—a, b, c, d, &c. . . . . l.
   Greatest variation in temperature during a single obser-
   vation = ·01° C.
   Greatest variation in temperature during whole interval
   = ·03° C.
   Length of path employed, 50·28 centim.
   Ordinary watch used to determine time.
   Mean temperature, 18°·28 C.

Mass.	Mean temp.	Time.	Time corrected to 18°·28 C.	$v^{\frac{3}{2}}$.	Mass, m.
	$\overset{o}{}$	seconds.	seconds.		grm.
a	18·27	128·2	128·0	·2462	·003516
b	18·27	121·4	121·2	·2672	·003815
c	18·27	135·2	135·0	·2273	·003245
d	18·27	132·4	132·2	·2346	·003349
e	18·27	117·2	117·0	·2817	·004022
f	18·28	137·8	137·8	·2204	·003146
g	18·29	197·2	197·4	·1285	·001835
h	18·29	148·6	148·8	·1963	·002804
i	18·29	160·8	161·0	·1746	·002492
j	18·29	131·2	131·4	·2367	·003380
k	18·29	136·0	136·2	·2244	·003204
l	18·29	157·8	158·0	·1795	·002564
				$\Sigma = 2\cdot6174$	$\Sigma = \cdot037372$

Taking

$$\sigma = 13\cdot59 \quad \text{and} \quad \rho = 1\cdot26,$$
$$g = 981,$$
$$\mu = 83\cdot9 \times 12\cdot33 \left(\frac{M}{13\cdot59 \times 2\cdot617} \right)^{\frac{2}{3}},$$
$$= 10\cdot69 \text{ for the mean temperature } 18^{c}\cdot28 \text{ C.}$$

B. Mass of mercury taken, ·1096 grm. This was divided into
   10 parts.
   Greatest variation in temperature during a single obser-
   vation = ·07° C.
   Greatest variation in temperature during whole experi-
   ment = ·22° C.
 (This result is therefore not so reliable as the previous one.)
   Mean temperature, 4°·35 C.
   Siemens chronograph employed to measure time.
   Length of path employed, 50·28 centim.

Mass.	Mean temp.	Time.	Time corrected to $4°\cdot35$ C.	$v^{\frac{3}{2}}$.	Mass, m.
	$°$	seconds.	seconds.		grm.
a	$4\cdot30$	$111\cdot6$	$111\cdot1$	$\cdot08401$	$\cdot01080$
b	$4\cdot32$	$101\cdot4$	$101\cdot1$	$\cdot09680$	$\cdot01244$
c	$4\cdot45$	$116\cdot1$	$117\cdot2$	$\cdot07751$	$\cdot00996$
d	$4\cdot28$	$123\cdot1$	$122\cdot4$	$\cdot07265$	$\cdot00934$
e	$4\cdot41$	$99\cdot8$	$100\cdot4$	$\cdot09782$	$\cdot01257$
f	$4\cdot48$	$150\cdot5$	$152\cdot3$	$\cdot05236$	$\cdot00673$
g	$4\cdot23$	$89\cdot75$	$88\cdot77$	$\cdot11760$	$\cdot01512$
h	$4\cdot32$	$107\cdot4$	$107\cdot1$	$\cdot08876$	$\cdot01141$
i	$4\cdot40$	$108\cdot3$	$108\cdot8$	$\cdot08667$	$\cdot01114$
j	$4\cdot50$	$114\cdot3$	$115\cdot9$	$\cdot07885$	$\cdot01014$
				$\Sigma = \cdot85303$	$\Sigma = \cdot10965$

Thus $\qquad\qquad \mu_{4°\cdot35\,\text{C.}} = 46\cdot27.$

The value of $\Sigma v^{\frac{3}{2}}$, when no corrections are made for temperature, is found to be

$$V^{\frac{3}{2}} = \cdot85434,$$

which agrees fairly well with the above result.

The temperature-variation of viscosity is considerable. It is of practical importance in certain applications, as, for example, in the use of viscous liquids for lubricating purposes. A special piece of apparatus was used by the author to investigate this variation for different liquids.

It consists of a glass tube closed at each end, with a lateral tube fixed at right angles to its middle portion and forming an outlet. The vessel is filled with the liquid and a very minute sphere of mercury is inserted. A thermometer passes through a stopper that encloses the liquid, the bulb of the thermometer reaching just up to the main tube. The vessel is immersed in a copper water-bath so that the main tube is vertical and the thermometer horizontal. The thermometer passes out of the bath through a small stuffing-box on one side. A window of glass is inserted in the opposite side of the bath through which the motion of the mercury may be observed. As soon as the mercury has fallen to one end of the tube, it is reversed and the mercury allowed to fall down to the other end again.

The thermometer reads the temperature of the viscous liquid at its middle, this being very nearly the mean temperature. The bath is heated slowly to about $50°$ and then

allowed to cool, during both of which operations the times of descent of the mercury from one fixed mark to another are carefully noted through the window, the water being stirred constantly. The times of descent are proportional to the viscosities, if a slight correction be made in each case for the variation in the densities of the mercury and the liquid, with change of temperature.

To illustrate the nature of this correction let us take the case of glycerine,

$$\mu = k \frac{(\sigma - \rho)}{\sigma^{\frac{2}{3}}} \text{T},$$

where T is the time of falling, and σ and ρ are the densities of mercury and glycerine respectively.

If s and r are the corresponding coefficients of expansion,

$$\mu = k \frac{(\sigma_0 - \rho_0) - t(\sigma_0 s - \rho_0 r)}{\sigma_0^{\frac{2}{3}}} (1 + \tfrac{2}{3} st).$$

This is approximated by taking $s = \dfrac{1}{5500}$ and $r = \dfrac{1}{1000}$,

$$\mu = \text{K}(12 \cdot 34 + \cdot 0002\, t)\text{T}.$$

The correction is therefore unnecessary between 0° and 30°, and is only 1 in 1200 from 30° to 70°. For ordinary temperatures it may therefore be neglected.

With a relative viscosity-curve thus obtained, and with one good absolute determination, we have the means of calculating the absolute viscosity at any temperature along the range.

Conversely, we have the means of estimating small masses of mercury by their speed of flow through glycerine or any other known liquid at a known temperature, or of estimating the mean temperature of the liquid.

For example, if a column of liquid be heated from above till its state of temperature becomes constant without the aid of convection, we can here determine the temperature-curve along its length, and in fact employ Forbes's method to determine the thermal conductivity of the liquid at various temperatures.

In concluding this description of the methods now being employed for the determination of absolute and relative viscosities, it may be well to remark on the advantages and disadvantages of these methods that have already manifested themselves. In the first place we are dealing with steady motions, and are able to investigate the phenomena attending

a constant rate of shearing in the liquid much more satisfactorily than if we observe an oscillating motion such as that of Coulomb's disk or Helmholtz's sphere. The existence of sliding-friction can be directly tested, not only between mercury and the more highly viscous liquids, but also between any two liquids that do not dissolve each other. Thus spheres of water may be used with nearly all the fixed oils, and spheres of oil of cloves (density 1·0475) or of oil of myrrh (density 1·0189) may be used with water.

The apparatus is simple and inexpensive; results may be rapidly obtained when a few standard mercury spheres are preserved. They should be kept in a sample of the viscous liquid to be tested. If a sphere breaks, the pieces should be washed in water and reunited on hard pressed blotting-paper. The quality of oils is often tested by their viscosity, and special viscosimeters on the capillary-tube principle of Poiseuille are used for the purpose. A time-reading through a sample of the oil with a standard mercury sphere offers an expeditious way of testing. If the oil is thin and the mercury falls too fast, a calibrated water sphere may be used instead. A sphere of water of 1 millim. radius, coloured with eosin to be clearly visible, travels at the rate of one inch per hour in castor-oil at 8° C.; and here in parenthesis it may be added that we have by far the simplest method of observing the time-integral of temperature for small ranges.

The general method cannot be employed for opaque liquids, as we wish to observe the falling sphere; but it is probable that with a little ingenuity this difficulty could be overcome if the opaque liquid presented itself for examination. The small inertia of the falling sphere, advantageous as it is in exhibiting the slightest variations of temperature, is a serious objection if small solid particles are held in suspension in the liquid. As a rule these particles will avoid the small sphere and not touch it; but in the event of contact occurring there is the likelihood of a permanent union between the two and of the particle being dragged down with the sphere, with consequent loss of speed of the latter. Hence clear liquids must be used.

The author wishes to acknowledge his obligations to Prof. Henrici for very kindly rendering available the apparatus of his laboratory for the needs of the above experiments.

XLIV. *The Attachment of Quartz Fibres.*
By C. V. Boys, *A.R.S.M., F.R.S.*[*]

MEMBERS of the Physical Society may remember that
in 1887 [†] I described a method of making fine fibres
of glass and other materials, but especially of melted quartz,
which latter had properties of great value, rendering them
more suitable for experimental work of combined delicacy
and accuracy than those of other known materials. Experi-
ments made since by others as well as myself have further
shown that for delicate work of the highest degree of accuracy
they are essential.

The method of fastening them, however, at their ends to
the pointed end of the torsion-pin at the top or of the
suspension below by shellac varnish, or better by melted
shellac, is apt to give rise, more especially if the fibre is
unskilfully laid in place so that it is twisted round the
point, to a slow creeping of the point of rest due to slow
changes in the shellac. This, except for the first few days,
can hardly ever be of an amount to seriously affect any ob-
servations; in fact I have made many observations of the
effect of gravitation between small masses with fibres so
fastened of a great degree of accuracy, besides those with the
radiomicrometer, pocket electrometer, &c., without any incon-
venience, yet I have felt that some method of attaching them
which would be less likely to hold the fibre by a part in a
state of torsional strain or of flexure would be preferable. If
the part of the fibre held could certainly be in its natural
position and state with respect to the rest, then, even if the
fastening should fail to be as perfect as a true weld, any
resulting change of zero should be small compared to that
observed where the portion held is twisted or much bent.

The process of silvering, electro-coppering, and soldering is
an obvious one, but it is not so easily carried out with a fair
degree of certainty and in a manner which is convenient of
application, as might be expected. My experience of last
autumn has enabled me to perform the process in a series of
operations, each simple enough, and, as far as I am able to
test it in the apparatus with which I am now measuring the
Newtonian constant of gravitation (which I may say is of
unusual delicacy), with perfect success. In this case the fibre
is necessarily stretched to not far from its breaking weight,

[*] Communicated by the Physical Society : read February 23, 1894.
[†] Phil. Mag. June 1887.

and it is in such cases that the stability of the fastening is most severely tried.

The first thing I found was that it was a mistake to solder the fibre to the torsion-rod and to the suspension directly. The difficulty of the manipulation is great and a change of fibre is very troublesome. The preferable plan is to solder the ends of the fibre to little tags of metal so small and light that they may be picked up by the fibre from anything on which they rest without risk of snapping the fibre at the point of junction. These tags, which are conveniently made of copper-foil, five millimetres long and one millimetre wide about at the wide end, tapering nearly to a point, can afterwards be fastened to the torsion support and the suspension by shellac varnish or by melted shellac, and now the enormous surface and the stiffness of the foil is sufficient to prevent any trouble from the causes to which reference has already been made.

These tags might also for some purposes, either or both of them, be made of T-form to hang in a pair of V's, and so dispense with cement altogether, and allow of the easy interchange of suspensions or of fibres, but I have not myself employed such a form.

The following operations are those which I have found to answer :—

1. Select a fibre of the right diameter to give the desired torsion. Since the torsion depends on the fourth power of the diameter, a small change in the diameter makes a fourfold change in the torsion, and great accuracy of measurement is needed where an exact torsional rigidity is required. Cut off a piece from two to three centimetres longer than will ultimately be required.

2. Fasten to the extreme ends of the fibre, with melted shellac, little weights of gold or platinum heavy enough to pierce a liquid surface.

3. Hang the fibre over a fixed round horizontal rod of wood, 1 centimetre in diameter or thereabouts, so that the little weights hang side by side, and lift up from below a little glass of strong nitric acid, so as to wet and clean the fibre well above the final points of attachment. The vessel must be wide enough to prevent capillarity from drawing the fibres to one side, or it must be brimful so that the surface is convex, which with nitric acid is objectionable. The vessel must be moved both upwards and downwards past the place at which the weights pass through the surface very rapidly, practically with a jerk; otherwise the weights will be drawn together by capillarity, and the fibres will get twisted,

or capillarity will give trouble somehow. With the rapid movement the little weights hardly acquire any pendular motion.

4. After a minute or two do the same, but to a slightly greater depth, with water which may be distilled.

5. When the acid may be supposed to be washed off, immerse in the same way in Rochelle salt silvering-solution (Kohlrausch, 'Physical Measurements,' p. 115).

6. Wash as in 4.

7. Fill a glass with the copper solution that is employed in electrolytic measurements of current, *i. e.* not saturated, and slightly acid. Dip the extreme point of the positive wire from a single cell into the liquid, and with a clean smooth negative wire take the hanging ends, one at a time, and having made the contact outside the glass by resting the upper part of the silver coat upon the wire, let down into the solution, keeping the fibre in gentle movement on the wire and making it dip more and less in the liquid. In a few seconds the little weight will be bright red, and the immersed portion of the silvered coat will be bright red also. The silver coat has sufficient resistance to prevent unduly rapid deposition. Do the same to the other end.

8. Cut off to length, allowing about 5 millimetres at each end for the junction. Take tags of copper-foil three or four centimetres long and three or four millimetres wide, tapering to a point, and having tinned the pointed end of each with the minimum of solder, again wet with chloride-of-zinc solution. On the wet surface lay the coppered end, taking care that it points in the right direction. Capillarity will now hold it. Rapidly heat the copper to the melting-point by holding a point about one centimetre from the narrow end over a minute flame. The solder will flash and envelope the coppered fibre. Cut off the tag of the desired length, holding the metal by the tag with a pair of pliers and not by the heavy end.

9. Wash in boiling water as in 4 to remove chloride of zinc. The fibre is now attached, but the protruding silver and copper give a want of definiteness in the place of attachment.

10. Dip up to the point of the tag in melted beeswax, following the precautions given in 3, but the two tags may be more conveniently dipped separately.

11. Dip up to the top of the copper and silver in strong nitric acid.

12. Wash in boiling water, which removes acid and beeswax and leaves the fibre ready for use.

13. If it is required to conduct electricity, as for instance to keep the needle of a quadrant electrometer electrically connected with a battery, the whole may now be silvered in a long tube and washed, otherwise it will insulate most perfectly. It may be mentioned here that for the most delicate possible electrometer, as I found in my experiments on the pocket electrometer, it is useless to expect to find any stability where a liquid surface is pierced. The only method of communicating with the needle is through a silvered quartz fibre. Owing to the insulating quality of a clean quartz fibre, delicate experiments are apt to be disturbed by unintended electrification of the suspension, and this may still remain after means have been employed to prevent it, for mere metallic contact between different metals leaves the surfaces in effect at different potentials, depending on the metals used, and, as I showed, in an idiostatic instrument the disturbance due to platinum and zinc is many hundred times the least that can be detected.

I have sought to reduce this form of error by either or both of two methods. In the first I make the inside of the chamber surrounding the suspension a figure of revolution, the axis being the line of the fibre; in the other, when possible, I make the surfaces of the suspension and of the enclosure one and the same, preferably electro-gilt.

The first method in very small instruments also in the main avoids what can no longer be safely neglected, as it has hitherto nearly always been, viz. gravitational attraction.

There is one more point which may be of some interest. If an unsilvered quartz fibre is threaded through a small hole in a thin metal plate, stretched by a suspended weight, and the hole is then wetted with chloride of zinc and soldered up, the fibre will, after washing off the fused chloride of zinc, pull out, leaving a hole fine and beautifully circular.

It is unnecessary to say more than I have already done, on more than one occasion, on the necessity for making the free space round a suspension in any instrument of extreme delicacy as small as possible and enclosing it by massive metal, itself protected from outside heating and cooling by a non-conducting cover, such as I have in the radio-micrometer; otherwise the convection currents set up in the free space will blow the suspension about, and produce vagaries which might be easily attributed to the fibre or its attachment. The disturbances due to this cause are apt to be much greater than anyone would at first imagine, and the small trouble spent in avoiding them in the manner indicated is well rewarded.

With regard to the manipulation with fine fibres, I have

already pointed out that the darkness inside a drawer just pulled out, if the operator is sitting at a table in front of a window with a good light, is such that fine fibres can readily be seen upon it as a background. No velvet or smoked surface or artificial blackness of any kind is comparable with it. On such backgrounds fine fibres are to all intents and purposes invisible. What is in many respects preferable to the dark background, at least in certain operations, is a plain looking-glass lying on the table. Fibres resting upon it become intensely brilliant and visible, provided the eye is so placed as not to see the sky light itself reflected from the mirror. One method of making the fibres very easily visible without influencing their torsion, is to smoke them with burning magnesium or arsenic. I do not suggest arsenic, but I mention it because of the very beautiful effect I once observed, after destroying all life in a small hot-house by burning a large quantity of bengal fire in which orpiment is a considerable constituent. All the spider-webs remained perfect with the spiders in their places as though alive, and the webs were of a dazzling white but perfect in form, undragged by the weight of the white arsenic upon them, thus contrasting strongly with the catenary distorted webs so much admired in frosty weather. It was this observation that suggested the magnesium smoking.

These last few points hardly come directly under the title of this paper, but I thought them worth adding as bearing upon the successful design of apparatus in which the full limit of delicacy and accuracy obtainable by the quartz fibre may be obtained, and upon the practical details of its treatment.

XLV. *A Method of finding the Refractive Index of a Liquid; applicable when the Liquid is not Homogeneous.* By T. H. LITTLEWOOD, *M.A.*[*]

Apparatus required.

THE chief piece of apparatus required for the method is a telescope with fixed wires in the eyepiece, arranged so as to be capable of motion along a horizontal scale, without changing its inclination to the vertical. The horizontal motion can be measured either by a vernier or by a micrometer-screw.

The liquid whose refractive index is to be determined is placed in a glass vessel about 3 feet away from the telescope, and with its level slightly below that of the telescope.

A scale of glass (or some material not acted on by the liquid) is placed vertically in the liquid and illuminated by monochromatic light. The position of the telescope on the horizontal scale is then taken when observing the various divisions on the vertical scale. From these readings the index of refraction can be ascertained.

First case.—When the liquid is homogeneous (fig. 1).

Fig. 1.

Suppose A, B are two points on the vertical scale out of the liquid; C, D two points within the liquid. Suppose a, b, c, d are the positions of the telescope on the horizontal scale when observing these points. Then Aa, Bb are parallel; and if CMc, DM$'d$ are the directions of the axis of the pencil of light from C and D, Mc, M$'d$ are parallel, and also CM, DM$'$ are parallel. Draw AN and CN$'$ parallel to $a\,b\,c\,d$. AN$=ab$, CN$'=cd$.

$$\therefore \tan \mathrm{AB}b = \frac{ab}{\mathrm{AB}}, \text{ and } \tan \mathrm{CDM}' = \frac{cd}{\mathrm{CD}}.$$

$$\therefore \mu = \frac{\sin i}{\sin r} = \frac{\sin \mathrm{AB}b}{\sin \mathrm{CDM}'} = \frac{ab}{cd} \times \sqrt{\frac{cd^2 + \mathrm{CD}^2}{ab^2 + \mathrm{AB}^2}}.$$

Second case.—When the liquid is not homogeneous (fig. 2).

Fig. 2.
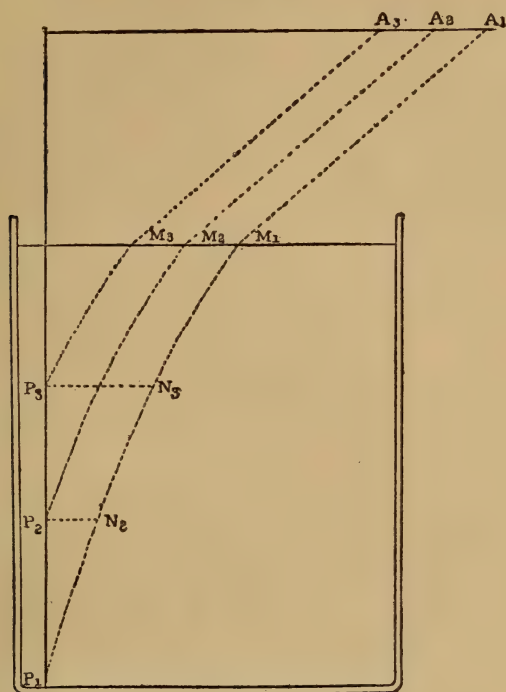
The liquid is supposed to have the same density at the same depth, which must be the case if it is at rest. The path of the axis of the pencil of light from any point on the scale which enters the telescope must be a curve.

Suppose P_1, P_2, P_3 various points on the vertical scale, and A_1, A_2, A_3 the corresponding positions of the inclined telescope when observing them. Suppose M_1, M_2, M_3 are the points where the axis of the pencil cuts the surface of the liquid, and draw P_2N_2, P_3N_3 parallel to the surface. Then it is clear that, since M_1A_1, M_2A_2, M_3A_3 are parallel, P_2M_2 is the same curve as N_2M_1 moved horizontally, parallel to itself, through the distance P_2N_2 or A_1A_2. P_3M_3 is the same curve as N_3M_1 moved through the distance P_3N_3 or A_1A_3. Similarly for other points.

Hence, by taking a number of points on the vertical scale and finding the corresponding positions of the telescope, and then plotting a curve having the vertical distances from the

lowest point for ordinates, and the observed distances through which the telescope has been moved from its first position as abscissæ, we can construct the path of the axis of the pencil through the liquid.

A previous observation of different points on the scale, before the liquid is poured into the vessel, gives the inclination of the telescope to the vertical, as in the first case. By measuring the inclination to the vertical of the tangent to the curve obtained, we can determine the refractive index at the various points of the liquid.

Assuming the curve for a short distance to be a straight line, the index of refraction of the layer of liquid between any two points can be calculated as in the first case, and a similar formula will be true.

XLVI. *Transformations of Mechanical into Chemical Energy.* (*Third Paper.*)   *Action of Shearing-Stress* (continued). *By* M. Carey Lea.

THAT mechanical energy may be transformed into chemical has been, I believe I may say, well proved by the reactions described in the previous papers of this series. But the matter is one of sufficient importance to make it desirable to accumulate evidence and to obtain a solid foundation of fact on which to rest the argument.

In the paper which described the effects of shearing-stress (Phil. Mag. Jan. 1894) I was able to cite one instance only in which the decomposition-product was obtained in easily weighable quantities. More lately others have been obtained, among them one, mercuric oxide, in which it can be determined how many units (gram-metres) of mechanical energy have been transformed into chemical.

Silver oxide precipitated and dried in the absence of daylight is soluble without residue in ammonia. After trituration, therefore, the unchanged portion is easily removed by that solvent.

1. Half a gram of silver oxide wholly soluble in ammonia was triturated for 20 minutes in a porcelain mortar, the unchanged portion was removed by ammonia, the residue was treated with nitric acid, filtered, and the silver thrown down by hydrochloric acid.

<div style="text-align:center">

Silver chloride obtained. . . . ·0402,

Corresponding to metallic silver . ·0303.

</div>

The use of a porcelain mortar is attended with the dis-

advantage that during the prolonged and forcible grinding necessary, a very appreciable amount of material is removed from the mortar and pestle which must be separated from the product subsequently. I have therefore made some comparative experiments with a large agate mortar and an agate pestle provided with a stout wooden handle adapted for the use of as much force as with a porcelain mortar. But even under the most favourable conditions, the efficiency of such a mortar is (as will be seen) only one fifth to one tenth that of a porcelain mortar of the same size. This is largely due, I think, to the high polish which is very unnecessarily given to the inside of agate mortars.

It is therefore better to make use of a porcelain mortar, taking adequate means afterwards to remove the material abraded.

2. The same quantity of silver oxide was triturated also for 20 minutes in an agate mortar. As the abrasion is inappreciable, it was only necessary to dissolve out the unchanged oxide with ammonia. There was left, metallic silver,

<p style="text-align:center">·0048,</p>

showing the much less efficiency of the agate mortar.

Mercuric Oxide.—The specimen taken was examined for its solubility in cold dilute (one tenth) hydrochloric acid, in which it dissolved slowly but completely.

Half a gram was taken, and after trituration the unchanged oxide was dissolved out by repeated digestions with hydrochloric acid. There remained mercurous chloride, a trace of metallic mercury, and, as a porcelain mortar was used, abraded porcelain. The reduction-products were dissolved out by a few drops of aqua regia, were filtered and precipitated by hydrogen sulphide.

Mercuric sulphide obtained . .	·0354
Corresponding to Hg	·0305
And to mercuric oxide	·0329

This, therefore (disregarding the traces of metallic mercury), is the amount of mercuric oxide which underwent reduction to mercurous oxide.

The oxidation of mercury to mercurous oxide and that of mercurous to mercuric are both exothermic reactions. As respects the thermic equivalent of the oxidation of mercury to both its oxides, quite different numbers have been found by different chemists. Nevertheless, if from these different numbers we calculate the amount of heat disengaged by the combination of Hg_2O with O, we get almost exactly the same figures whether we use Thomsen's results as modified by Nernst, or those of the French chemists; it matters little,

therefore, which are taken. Ditte, in his work *Les Métaux* (Fascicule ii. p. 500), adopts the numbers 21·1 and 15·5 respectively.

On this basis the amount of energy that must be supplied to convert $2\,HgO$ to $Hg_2O + O$ (endothermic) is that which corresponds to 9·9 great calories. Therefore 400 grams of mercury existing in the state of mercuric oxide will require that amount of energy supplied to reduce it to mercurous oxide. One gram, therefore, will require the equivalent of 24·75 small calories and one milligram ·02475.

In the experiment described mercurous oxide corresponding to 30·5 mgs. metallic mercury was obtained. The energy required to reduce 30·5 mgs. existing as mercuric oxide to mercurous corresponds to 0·755 water-gram-degree and this again to 321·5874 gram-metres. This number, therefore, 322 gram-metres, represents the mechanical energy transformed into chemical energy in the above operation.

Potassium Ferricyanide.—A good method of obtaining this salt absolutely free from ferrocyanide is to dissolve the commercial product in hot water and add a little potassium permanganate by degrees until the solution takes a faint reddish colour. Very little is usually required. The solution is then filtered and crystallized, taking the first crystals only.

Ferricyanide, purified in this way, was triturated about 20 minutes in an agate mortar. On adding water a deep green solution was obtained which, by standing and warming, let fall abundance of a blue powder.

Ferric Ammonia Alum.—A specimen of this salt which, when tested with potassium ferricyanide, gave a pale wine-coloured solution without a trace of green, was taken and 3 decigrams were triturated for 25 minutes in a porcelain mortar.

After trituration the ferrous salt formed distinctly reduced gold solution. A few drops of the dissolved substance being added to a solution of ferricyanide, changed it to an intense green colour. Undoubtedly reduction had taken place. It need scarcely be mentioned that in this case the tests should be applied immediately after the trituration. A few hours' interval completely changes the reactions owing to the reoxidation of the ferrous salt formed.

This experiment was repeated with additional precautions. To a strong solution of ferric ammonia alum enough potash permanganate was added to distinctly colour the liquid, which was then made to crystallize quickly by cold. These crystals, certainly free from ferrous salt, were then actively triturated in a porcelain mortar for 25 minutes. The filtered solution

produced immediate purple clouds in a cold, very dilute solution of gold chloride and an abundant blue precipitate in one of potassium ferricyanide.

It is essential that the ferric alum be thoroughly dried (at a temperature not exceeding 40° C.), otherwise, owing to the large quantity of water of crystallization, it will become pasty in grinding and then no reduction will take place.

Cupric Chloride.—Even by long trituration this salt showed no indication of reduction.

This reaction, taken with the preceding, shows how distinct is the action of mechanical energy from that of heat. For cupric chloride is reduced by heat to cuprous chloride, but shearing-stress has no such action. On the other hand, shearing-stress reduces ferric sulphate, which heat does not.

Sodium Chloraurate.—In the previous paper, the effect of triturating this salt in a porcelain mortar was given. For comparison it has since been tried in an agate mortar. With 20 to 25 minutes' trituration, 3 decigrams gave 2·7 milligrams metallic gold, showing, as in other cases, the much lower efficiency of the agate mortar.

Silver Carbonate.—Half a gram was triturated about 25 minutes in a porcelain mortar. It darkened much. The unaltered carbonate was dissolved out by exhausting repeatedly with ammonia. The residue was treated with nitric acid, filtered, and the silver thrown down by hydrochloric acid. It amounted to 11 milligrams, corresponding to metallic silver ·0083.

Silver Sulphite was precipitated in a dark room by alkaline sulphite and treated in the same manner as the foregoing. Silver chloride obtained ·0092, corresponding to metallic silver . . . . . . ·0069.

Silver compounds, although easily giving weighable results, are not well suited for determining the transformation of energy that takes place. It is probable that the reduction is to argentous salt, but it is not certain. Ammonia decomposes argentous salts into argentic salts that dissolve and metallic silver that remains. So that whether we consider the reduction as being to argentous salt or to metal, in either case we find the same quantity of metallic residue and cannot distinguish with certainty.

It scarcely needs to be said that the object of these various determinations is not to establish any relation between the quantity of substance taken and the amount of decomposition that ensues, for none exists. It often happens that when a larger quantity is taken there results a diminished decom-

position product, the particles protect one another.   And even when all other things are equal, the product will depend on the activity and dexterity with which the grinding is done.

But what is really important is that the amounts obtained enable us in particular cases to determine the exact amount of mechanical energy which has been transformed.

———————

In concluding this paper, two cases will be mentioned which do not belong to the above category, inasmuch as the reductions are exothermic.   As a general rule, to cause substances to part with oxygen, energy must be supplied, but there are exceptions.   Auric oxide, for example, disengages heat in parting with oxygen, and the same is the case with potassium permanganate.

Auric Oxide.—As just said, the reduction of auric oxide is exothermic.   Thomsen found the equations for its formation :

$$2\,Au + 3O + 3H_2O = 2\,Au\,(OH)_3 - 2 \times 6\cdot6.$$
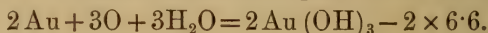
The production, therefore, of a molecule of auric hydroxide requires that $6\cdot6$ C. be supplied.   We should, therefore, expect to find gold hydroxide more easily and more largely reduced by shearing-stress than other oxides.

Experiment confirms this expectation, and although this case does not belong to the subject proper of this paper, which deals with endothermic reactions, it seems sufficiently interesting to add in this appendix.

Gold trioxide hydrate, $Au\,(OH)_3$, was obtained by Figuier's method (a gold solution is rendered strongly alkaline with potash or soda, and barium chloride is added as long as it causes a precipitate.   Part of the gold remains in solution. The barium aurate is washed and decomposed with very dilute nitric acid).   The brown powder after drying was ascertained to be completely soluble in warm dilute hydrochloric acid (1 to 10), showing that no gold had been reduced.

(1) Of gold oxide 155 mgs. were taken and were triturated 25 minutes in a porcelain mortar.   The large reduction was at once evident to the eye, the pestle looked as if plated with bright gold. The unchanged portion of oxide was removed by digesting with dilute hydrochloric acid.   The metallic gold was dissolved in aqua regia, reduced and weighed. It amounted to . . . . $\cdot0718$.

The 155 mgs. of gold oxide taken contained $123\cdot1$ of gold. The reduction was, therefore, as 718 to 1231.   Fifty-eight per cent., or more than half the gold contained in the material employed, was reduced.

(2) 200 mgs. gold oxide were triturated 30 minutes in a

porcelain mortar. After removing the unchanged oxide as above, the metallic gold was dissolved, filtered, and reduced.

Obtained . . . . . ·0538.

Potassium Permanganate.—Two molecules of permanganate by reduction to $2MnO_2H_2O$ lose 3 atoms of oxygen and at the same time 28·4 cal. The reaction is therefore exothermic.

By active trituration a portion of the permanganate taken easily undergoes reduction. Exhausted with water, a brownish-black insoluble residue remains, which dissolves with effervescence in strong warm sulphuric acid, forming a violet solution—the residue is therefore manganic peroxide.

Three estimations were made. A first rough one, after trituration for 25 minutes in a porcelain mortar, gave of washed and dried material which had become insoluble, 43 mgs.

The second was made on a like quantity of permanganate, also in a porcelain mortar. The portion rendered insoluble was dissolved in hydrochloric acid, and estimated as Mn_3O_4.

Quantity obtained . . ·0136,

showing that 28·25 mgs. of permanganate had been reduced to MnO_2.

The same quantity of permanganate treated in the same way in an agate mortar gave only ·0030 MnO_2, owing to the less efficiency of the mortar.

The reduction in the case of these last two substances are exothermic ; they, however, do not take place spontaneously, but require the aid of an exterior force—this aid is supplied by shearing-stress.

In these three papers a large number of reactions have been described in which mechanical energy has been transformed into chemism. The number might be extended, but in practice is necessarily limited to those cases in which a perfect separation can be made between the original substance and the altered product.

XLVII. *The Origin of the Theory of Solutions.*
By J. H. van't Hoff[*].

I. *Historical Introduction.*

WHEN I was requested to deliver an address before the German Chemical Society summarizing the work which I had done in the realm of physical chemistry, it

occurred to me that I might conveniently start from one of two centres. It was open to me to give an account either of the investigations on double salts and the limits of their existence, or of the theory of dilute solutions and osmotic pressure. As I had no desire to introduce a topic which might prove unwelcome to the members of the Society, I remitted the choice of the subject to the committee. Although I had half hoped it would be otherwise, they expressed themselves in favour of the theory of solutions, but in giving an account of this subject I have promised to avoid everything of a polemical nature. Another reason which would have induced me to eschew this subject is that, in outline at least, it is already familiar to most of you ; consequently, a simple exposition would be mere repetition. I think, therefore, that it would be better to consider for a short time the origin of the theory of solutions ; not for the purpose of espousing claims of priority, but rather to disclose how the train of ideas developed in my mind, so that finally the opponents can also say " Dass alles wissen, alles vergeben ist."

All my opinions in regard to the " position of the atoms in space," which were only a structure founded on the relationship between a *physical* property, viz. optical activity, and chemical constitution, began to germinate when I commenced the study of chemistry under Kekulé and Wislicenus. Young as I was at that time, I wished to determine the relation between constitution and *chemical* properties, for a constitutional formula should express the complete chemical behaviour of a substance.

This was the origin of my work *Ansichten über die organische Chemie*, which is possibly not known to you. It little matters. It was only of value to me in so far as it clearly indicated a gap in our knowledge. As is well known, the oxygen in organic compounds exercises an accelerating action on almost all changes ; for example, the oxidation of methane is more difficult than the oxidation of methyl alcohol, and so on.

An accurate knowledge of the velocity of reactions was thus rendered necessary, and this consequently gave rise to my work *Études de dynamique chimique*. The study of chemical equilibrium, which depends on the equality of two opposed reactions, naturally accompanied that of the velocity of reaction, and was placed on a sure basis by its connexion with thermodynamics. As often happens, in trying to reach my goal I was getting farther and farther from it. And since the question of equilibrium is intimately connected with the problem of chemical affinity, I first of all encountered a

very simple phenomenon of affinity, namely the attraction for water.

Mitscherlich (*Lehrbuch der Chemie,* 4th edit. 1844, p. 565) had already inquired into the magnitude of the attraction which Glauber's salt has for its water of crystallization, and perceived a measure of it in the diminished pressure of the water of crystallization. He says (*loc. cit.*), " If Glauber's salt be introduced into a Torricellian vacuum at 9°, the mercury sinks 2·5 lines (5·45 millim.) by the liberation of aqueous vapour. On the other hand, water itself causes a fall of 4 lines (8·72 millim.). Hence the affinity of sodium sulphate for ts water of crystallization corresponds to the difference, 1·5 line (3·27 millim.), *i. e.* about $\frac{1}{16}$ of a pound ($\frac{1}{32}$ kilog.) per square inch (2·615 square centim.)."

This value, $\frac{1}{200}$ of an atmosphere, seemed to me excessively small, and I still retained the opinion, which I had obtained from Helmholtz's Faraday Lecture, that even the weakest chemical forces are exceedingly great. It was therefore desirable to see if this attraction for water could be more directly measured in still simpler cases ; in aqueous solution, for example, we have probably a much simpler phenomenon than the attraction for water of crystallization. Whilst pondering over these questions I met my colleague de Vries and his wife as I was leaving the laboratory. De Vries happened to be occupied with osmotic experiments, and called my attention to Pfeffer's determinations.

You are all familiar with the apparatus which Pfeffer used. It consisted of a porous pot, the wall of which was rendered semipermeable by precipitating in it a layer of copper ferrocyanide. This semipermeable membrane, which allowed water but not a dissolved substance, for instance sugar, to pass through, admitted of the measurement of the osmotic pressure, which amounted in the case of a 1 per cent. sugar-solution to two thirds of an atmosphere.

This pressure was exceptionally great when compared with Mitscherlich's number, but there is nevertheless a relationship between them.

If in fig. 1 we suppose the sugar-solution contained in the lower left-hand side and separated from the water on the right side by means of a semipermeable membrane, then the water will pass from right to left until the pressure reaches the amount observed by Pfeffer. In the space above the liquids, however,

Fig. 1.
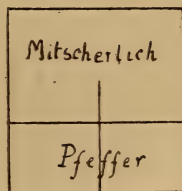
the water-vapour passes in the same direction, but only until the pressure reaches that measured by Mitscherlich.

It is even possible to make a calculation founded on this interdependence. The force with which Mitscherlich dealt is small because it acts on the attenuated vapour, whilst that of Pfeffer is large because it refers to the concentrated water. Thus we have:—

$$\text{Pfeffer : Mitscherlich} = 1000 : \frac{p}{760}\, 0.08956\, \frac{18}{2}\left(1 + \frac{1}{273}t\right),$$

so that we can calculate Pfeffer's force from the diminution of vapour-pressure (freezing-point).

Temperature.	Osmotic Pressure.	0·00239 T.
6·8	0·664	·668
15·5	0·684	0·689
22	0·721	0·704
32	0·716	0·728
36	0·746	0·737

The above proportionality is not quite exact. The accurate formula is obtained if the work which the attraction for the water can perform is made the starting-point; this is independent of the fact whether the water as such, or its vapour, is transferred. Hence we get the relation for 18 kilos water,

$$2\mathrm{T}l\,.\,\frac{p_w}{p_l} = \frac{1}{423}\mathrm{PV};$$

where p_w and p_l represent the pressure of the water and the solution respectively, P the osmotic pressure in kilos per square metre, and V the volume in cub. centims. of 18 kilos of water.

This formula reproduces Pfeffer's results very exactly. It also lends itself for the determination of the pressure when p only is known; so that we have the solution of Mitscherlich's problem in regard to the water of crystallization, for obviously this attraction for water corresponds to that of a solution having an equal maximum vapour-pressure. Hence we get:—

Substance.	Temperature.	Pressure.
$SO_4Na_2 . 10H_2O$......	$\overset{\circ}{9}$	600 atm.
$SO_4Fe . 7H_2O$.........	25	510 ,,
$SO_4Fe . 7H_2O$.........	65	245 ,,
$SO_4Cu . 5H_2O$.........	50	1100 ,,
$SO_4Cu . 3H_2O$.........	...	1730 ,,

i. e. in order to prevent Na_2SO_4 from taking up its water of crystallization, for example in Pfeffer's apparatus, a pressure of 600 atmospheres at 9° is necessary and sufficient.

We must now return from Mitscherlich's affinity problem of the attraction for water of crystallization, where we are obviously dealing with enormous concentrations, to the question of dilute solutions. Hitherto I have been drawing your attention to what appeared in my *Études de dynamique chimique*, and now I would like to refer to a publication in the *Archives Néerlandaises*. There I gave the proof of my equation,

$$\frac{dl\mathrm{K}}{d\mathrm{T}} = \frac{q}{2\mathrm{T}^2},$$

which also occurred in my *Études*.

The introduction of this equation here is only of secondary importance. The chief point to be noted is, that I was able by means of reversible cycles to deduce this equation for dilute gas systems. I should now like to show its applicability to dilute solutions.

It occurred to me that all the reversible cycles which so greatly simplify the use of thermodynamics in treating of gases, are also applicable to dilute solutions, provided that a semipermeable wall is employed, as may be seen from the following figure.

This was a decided advance, and it clearly followed that the osmotic pressure for dilute solutions must obey Gay-Lussac's law, or, in other words, must vary with the temperature in the same way as the gas-pressure. A direct comparison is simplest.

The left side of the figure represents the well-known cycle for a gas. The heat supplied at T which for dilute gases corresponds only to the external work $P\Delta V$, on lowering the temperature by $d\mathrm{T}$ is represented by the work $Vd\mathrm{P}$.

On the right side the osmotic pressure P_0 is chosen equal to P ; the cylinder is semipermeable and plunged in water,

Fig. 2.
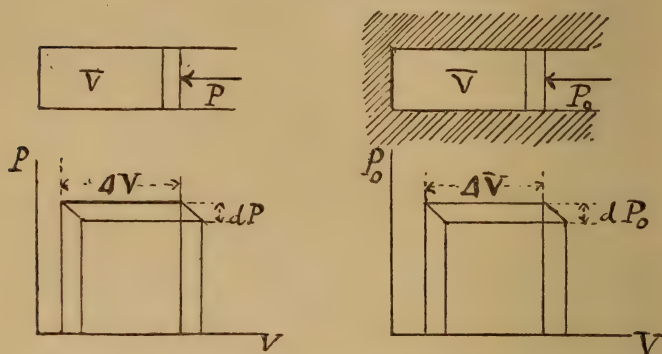
the increase in volume, again ΔV, then corresponds (for dilute solutions where the heat of dilution is zero) only to the external work $P\Delta V$. Now here the same lowering of temperature $d T$ must correspond to the same work $V d P_0$, so that we have $d P_0 = d P$. Incidentally it may be remarked that such cycles take a very simple form when V is so great that ΔV produces no appreciable change of pressure. On the other hand, $d P$ is so small compared with ΔV, that the course of the adiabatic may be neglected.

This result, Gay-Lussac's law for dilute solutions, was quite in agreement with the available numerical data, although it could not be asserted that it was sufficient to constitute a proof. A glance at the table containing Pfeffer's results with a 1 per cent. sugar-solution shows this.

But there is also a second relationship, the full significance of which was almost recognized by Pfeffer, viz., that the osmotic pressure in dilute solutions is proportional to the concentration ; that is to say, that Boyle's as well as Gay-Lussac's law is applicable to dilute solutions. The mathematical expression for both laws is

$$PV = RT,$$

and with its help I was enabled to prove the above thermo-dynamical formula, and so my goal was reached.

On calculating the value of R, however, the result was quite unexpected. It is well-known that for kilogramme-molecules of gases the value of R is constant and equal to about 846, provided that P is expressed in kilogrammes per square metre and V in cubic centimetres. We have already

seen that Pfeffer found the osmotic pressure of a 1 per cent. sugar-solution at 6°·8 to be 0·664 atmosphere.

We have, therefore,

$$P = 0·664 \times 10333, \qquad V = 34·2, \qquad T = 279·8.$$

Hence $R = 840.$

At first I thought this was a pure accident, and was disinclined, at least in the case of sugar, to attach any physical meaning to this result. Equality of both values of R, *i. e.* for gas and solution, has only one meaning however, viz. that the sugar exerts an osmotic pressure equal to the pressure which gaseous sugar of the same concentration and at the same temperature would exert.

In other words, this is the application of Avogadro's law to sugar-solutions, the only difference being in the substitution of osmotic pressure for ordinary gas-pressure.

II. *The Theory of Dilute Solutions.*

Although the above remarkable equality of osmotic and gas-pressure at equal molecular concentration and temperature appeared at first to be a mere chance, yet it occurred again and again, and was connected with so many known and afterwards with newly discovered regularities, that at last there seemed to be no room left for doubt.

De Vries was the first to determine successfully the molecular weights of substances in solution by an application of the extended Avogadro's law. According to Loiseau-Scheibler the molecule of raffinose contained 18 atoms of carbon, C_{18}, whilst Berthelot gave it a formula with C_{24}. In order to settle the question, a comparison was made with sugar, and from each substance a few isotonic solutions were prepared, *i. e.* solutions having equal osmotic pressures. This was accomplished in an extraordinary manner with the help of plant-cells containing protoplasm. The membrane of the protoplasm is semi-permeable, and when the cells are placed in solutions having greater osmotic pressures, the protoplasm contracts and separates from the cell-wall, or what is termed plasmolysis takes place. If the solution has a lower osmotic pressure than the contents of the cell, the protoplasm continues to fill the cell completely. The point at which the protoplasm just begins to recede from the cell-wall when it is placed in solutions of sugar and raffinose is sought out, and the solutions thus proved to be isotonic. It is then only necessary, as in the case of gases, to determine the ratio of the amounts of sugar and raffinose contained in equal volumes of the

solutions in order to calculate the molecular weight. In this way it was found that the formula of raffinose contained C_{18}. This conclusion has since been confirmed by the splitting up of raffinose into equal quantities of the three sugars—glucose, levulose, and galactose,—each containing six atoms of carbon.

We will now consider the laws associated with osmotic pressure.

The Lowering of the Vapour-Pressure. — If we suppose, with Arrhenius, that we have osmotic equilibrium with a 1 per cent. sugar-solution, as in fig. 3, where H is the rise due to osmotic pressure, then the column of solution H represents the osmotic pressure and the column of vapour H the lowering of the vapour-pressure. Hence, for any solvent whatever, we obtain, as before,

Fig. 3.
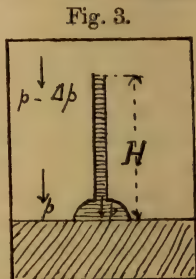
$$\frac{\text{Lowering of vapour-pressure}}{\text{Osmotic pressure}} = \frac{0 \cdot 08956 \frac{M}{2} \cdot \frac{\text{Vapour-pressure}}{760}}{1000\, s},$$

where s represents the specific gravity of the solvent and M its molecular weight in the gaseous state.

Should the osmotic pressure be equal to the gas-pressure, then, by comparison with hydrogen, it will be

$$\frac{10\, s}{0 \cdot 08956 \frac{m}{2}} \cdot 760$$

for a 1 per cent. solution of a substance having the molecular weight m. Hence

$$\frac{\text{Lowering of vapour-pressure}}{\text{Vapour-pressure}}\, m = 0 \cdot 01\,M.$$

This is the well-known law of Raoult, which states that the molecular relative lowering of vapour-pressure is equal to $\frac{1}{100}$ of the molecular weight of the solvent.

It is to be noted that here, as in all laws relating to dilute solutions, we have only a limiting law which strictly applies to infinitely dilute solutions, where the accurate expression of the above law becomes

$$\frac{dp}{p\,dm} = M.$$

The following table contains the results obtained with fairly dilute solutions.

Formula.	M.	Relative molecular lowering of vapour-pressure.
H_2O	18	0·185
PCl_3	138	1·49
CS_2	76	0·8
CCl_4	154	1·62
$CHCl_3$	120	1·3
C_5H_{10}	70	0·74
C_6H_6	78	0·83
ICH_3	142	1·49
CH_4O	32	0·33
$C_4H_{10}O$	74	0·71
Hg	200	2 (Gallium).

The Raising of the Boiling-Point.—Fig. 4 contains portions of the vapour-pressure curves for solvent and solution. The

Fig. 4.
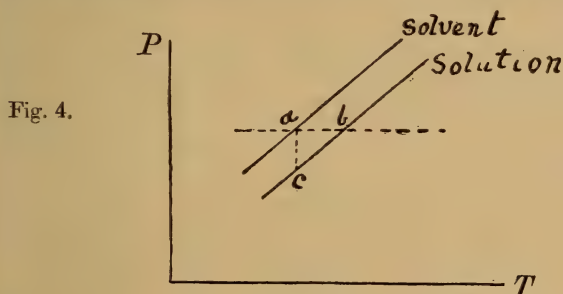
horizontal line ab corresponds to the atmospheric pressure, a is the boiling-point of the solvent, b that of the solution, ab the rise of boiling-point (dT), and ac the lowering of vapour-pressure (dp).

If, in the well-known equation

$$\frac{dlp}{dT} = \frac{q}{2T^2},$$

where q represents the latent heat of evaporation per kilogramme-molecule, the above expression of Raoult's law,

$$\frac{\Delta p}{p} m = 0\cdot01\,M,$$

is introduced, we obtain

$$m\Delta T = \frac{0\cdot02\,T^2}{q/M} = \frac{0\cdot02\,T^2}{W},$$

or, rigorously,

$$m \cdot \frac{dt}{dm} = \frac{2T^2}{W},$$

which is the well-known van't Hoff-Beckmann-Arrhenius expression for the molecular rise of boiling-point, the experimental confirmation of which is contained in the following table (W = the latent heat of evaporation per kilogramme).

Substance.	$\dfrac{0 \cdot 02\,T^2}{W}$.	Beckmann (found).
$CHCl_3$	36·6	37–39
CS_2	23·7	23–25
$C_2H_4O_2$	25·3	25–26
C_2H_6O	11·5	11–13
$C_2H_3O_2C_2H_5$	26·1	27
$(C_2H_5)_2O$	21·1	20–22
H_2O	5·2	5–5·6
$(CH_3)_2CO$	16·7	16–17

The Lowering of the Freezing-Point.—Similarly, $\dfrac{0 \cdot 02\,T^2}{W}$ represents the molecular lowering of the freezing-point, and reference may be made to a memoir read before the Swedish Academy, where I first described Avogadro's law for solutions as a " propriété curieuse de la matière diluée," along with a confirmation of Raoult's so-called Normal Numbers.

Substance.	W.	T.	$0 \cdot 02\,\dfrac{T^2}{W}$.	Raoult.
H_2O	79	273+ 0	19	28·5
$C_2H_4O_2$	43	273+17	39	38·6
CH_2O	56	273+ 9	28	27·7
C_6H_6	29	273+ 5	53	50
$C_6H_5NO_2$	22	273+ 5	70	70·7

Before publishing the above memoir I took the precaution to ask Prof. Petterson if he would determine the latent heat of fusion of ethylene bromide, which I had predicted, from the consideration of Raoult's data, would be 13. This prediction was found to be correct, and has since been confirmed in a great many cases, especially by Eykman.

The following table contains the calculated and found values for the latent heat of fusion :—

Substance.	Calc.	Found.	Substance.	Calc.	Found.
Lauric acid	44	45	Thymol	27	28
Naphthalene.........	36	36	Urethane	41	41
Phenol	25	26	N_2O_4	33	34
p-Toluidine	39	39	$ICl\,a$	16	16
Diphenylamine ...	21	24	$ICl\,\beta$	14	14
Naphthylamine ...	20	26	Hg	2·8	2– 3
Diphenyl	28	29	Sn	13	14–17
Azobenzene	29	29			

Unfortunately I have no more time at my disposal to follow out all the other relationships which are founded on the assumption that R = 846, so that the following tabular survey must suffice :—

Law of the coefficients of distribution (Berthelot-Nernst).

Pfeffer-de Vries.
$$P = \frac{846\,T}{V}.$$

Isotony.

Boyle's and Gay-Lussac's Law for osmotic pressure.

Henry's Law.

Lowering of vapour-pressure.

Raoult.
$$\frac{\Delta p}{p}\, m = 0{\cdot}01\ M.$$

Application to Gases. Avogadro.

Guldberg and Waage's Law.

$$\frac{d\,l\,k}{dT} = \frac{q}{2\,T^2}.$$

Beckmann-Arrhenius.
$$\frac{0{\cdot}02\,T^2}{W}.$$

Boiling-point.

Determination of molecular weight in solution.

Application to Solutions. van't Hoff.

van't Hoff-Eykman.
$$\frac{0{\cdot}02\,T^2}{W}.$$

Freezing-point.

Avogadro-van't Hoff Law.

III. *Deviations.*

The question now arises, Is the foregoing sketch to be considered as a theory of solution?

Not necessarily. It is rather a necessary correlation of experimental results and laws, some of which have been known for a long time, whilst others are of quite recent origin, and I scarcely think that serious objections can be raised against this correlation.

It is not even necessary to select osmotic pressure as the starting-point; the whole may be just as easily deduced from Henry's or Raoult's law, but the osmotic law is a simple tangible expression of the whole behaviour of dilute solutions, and its physical meaning can be easily stated in words, and graphically represented.

When rarefied matter exists under such conditions that it tends to spread itself out by diffusion, then the pressure, at any given temperature, which prevents it from so doing depends only on the number of molecules and is independent of their nature and of the medium in which they exist.

Where does the theory of solutions begin? In my opinion it begins where the attempt is made to explain the deviations as being due to secondary causes.

Such deviations exist, and immediately show themselves by non-agreement with all the above correlated laws, for example, in abnormal values of the osmotic pressure, deviations from Henry's law, unexpected lowerings of freezing-point, &c.

In now passing on to the real theory of solutions, my object is to mention shortly in what way these deviations have been explained, and with what success.

One thing in particular is to be noted: the above-mentioned relations, if they are to remain at all valid, necessitate only that we are dealing with great dilutions, and are thus limiting laws like those of Boyle, Gay-Lussac, and Avogadro. But it is well-known that exceptions are also to be met with in the case of very dilute solutions. Some lowerings of the freezing-point are unexpectedly small, whilst others are unexpectedly great. That this does not go so far as to conceal the main laws is best proved by the fact that Raoult, long before the theory of solutions, always referred to the present calculated values as " normal."

The Small Lowerings of the Freezing-point, corresponding to a smaller osmotic pressure, are of two kinds.

First, and especially in the case of compounds containing the hydroxyl group, *e. g.* the alcohols and acids in benzene solution, values are obtained which are obviously only about

one half of the normal value. These exceptions are explained at once by the formation of double molecules; and this explanation has been confirmed by the fact that such solutions on dilution often lead to normal values, as if a dissociation of the double molecules took place.

Secondly, it has long been known that some acids, *e. g.* formic and acetic acids, seem to have a bimolecular structure even in the gaseous condition.

Finally, and quite recently, Ramsay and Shields have, by a method which is not far removed from osmotic pressure, come to the important conclusion, similar to the above, that alcohols and acids, in contradistinction to the hydrocarbons, possess a polymolecular constitution; and I have grounds for suspecting that, if Ramsay slightly altered his method of calculation, a still better agreement would be obtained.

There is still another case, where small lowerings of the freezing-point are observed, which cannot be explained by a polymolecular constitution because simple halving is not shown and because even a rise in the freezing-point often occurs, as in solutions of antimony in tin, naphthol in naphthalene, carbazol in phenanthrene.

Then the idea occurred to me that the dissolved substance as well as the solvent were frozen out together.

Fig. 5 represents the vapour-pressure of ice and water near the freezing-point, *a*, and also the vapour-pressure of a

Fig. 5.
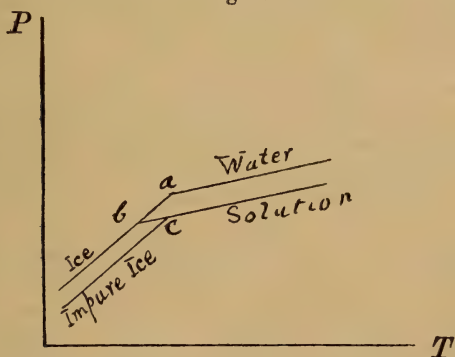
solution whose freezing-point lies at *b*. If now the ice is able to carry down some of the dissolved body, its vapour-pressure diminishes, and the freezing-point correspondingly rises to *c*, and can even lie to the right of *a*. As a matter of fact, experiment has repeatedly confirmed this assumption, as *e. g.* with solutions of lead, cadmium, tin, and gold in

mercury (Tammann), thiophene in benzene, antimony in tin, naphthol in naphthalene (van Bylert), indol in naphthalene, carbazol in anthracene (Ferratina and Garelli), and also with ketopentene derivatives.

According to Ferratina and Garelli it would appear that a too small lowering of the freezing-point is a simple means for determining the constitution of a substance, as the freezing out of the dissolved substance is very often to be inferred from similarity of constitution. In this way it was shown, *e.g.*, that nicotine probably was not a dipyridyl derivative, and this is confirmed by the work of Pinner and Blau.

Abnormally Large Depressions of the Freezing-point.—To return once more to the osmotic experiment of de Vries. The so-called isotonic coefficients, which are obtained by comparison of isotonic solutions, express the relative osmotic force in solutions which contain the same number of molecules in equal volumes, or, in other words, the relative osmotic force of molecular quantities.

The so-called isotonic coefficients, which occur in so many physiological experiments as conditional factors, should according to the theory be equal to unity; they are thus obviously of serious importance in the development of a "theory of solutions" and have imposed on me, in my Swedish memoir, a certain amount of restraint in speaking of a remarkable property frequently occurring in rarefied matter.

Since that time, however, the state of affairs has altered. Arrhenius has shown that the abnormally high values occur only in solutions which conduct electricity, and numerous reasons have been adduced to explain the abnormally high values in consequence of the presence of ions obtained by the splitting up of the molecules in solution. In the following table I give the numbers which have been obtained in some of the most significant cases, and a glance suffices to show what has already been attained in this way:—

Substance.	Isotonic coefficient found.	Do. calculated from the conductivity.
KCl	1·81	1·85
NH_4Cl	1·82	1·84
$Ca(NO_3)_2$	2·48	2·46
LiCl	1·92	1·84
$MgCl_2$	2·8–2·3	2·48
$MgSO_4$	1·2–1·4	1·35
$FeCy_6K_4$	3·09	3·07
$Co_2Cy_{12}K_6$	6·02	5·93
Seignette's salt	1·2	1·37
Tartar-emetic	2·47	2·39

Does, then, this assumption of electrolytic dissociation correspond to actual fact? I am just about to allude to this matter, and I ask the continuance of your attention for a short time in order to show what has followed from a consideration of the narrow but important domain of saponification.

In 1883, in conjunction with Reicher, I carefully investigated the velocity with which bases saponify esters. The first experiments were made with soda and potash, and then we tried calcium hydrate, as we expected a different velocity of reaction. The corresponding equations are

$$KOH + CH_3CO_2C_2H_5 = CH_3CO_2K + C_2H_5OH,$$
$$CaO_2H_2 + 2CH_3CO_2C_2H_5 = (CH_3CO_2)_2Ca + 2C_2H_5OH.$$
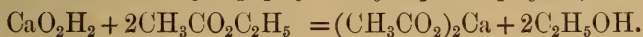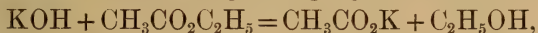
Proportionality between the velocity of reaction and the square of the concentration of the ester in the latter case, and with the concentration alone in the former, might be expected, but we found in both cases practically the same velocity:

Potash 2·298; Calcium hydrate 2·285.

This curious fact immediately found its explanation in the theory of electrolytic dissociation, for the reaction in both cases is conditioned by the hydroxyl alone, and hence is represented by the equation

$$\overset{-}{O}H + CH_3CO_2C_2H_5 = C\overset{-}{H_3}CO_2 + C_2H_5OH.$$
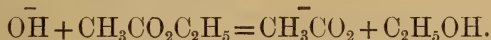
Ostwald observed an analogous fact, viz., that greatly diluted acids have the same velocity of saponification. In this case, the action is conditioned by the presence of hydrogen ions.

Quite recently Wijs has, in my laboratory, investigated the saponifying action of water itself.

This investigation possesses new interest on account of the question whether the excessively small saponifying power of water is due to the presence of the minute quantity of hydroxyl and hydrogen ions.

In this case the question is experimentally and theoretically somewhat more complicated. Experimentally, the action of water is disturbed immediately after the commencement of the saponification by the co-operation of the acid which is formed, and hence must be measured only at the beginning. Theoretically, the increase in hydrogen ions, on account of the formation of acid, must be taken into account in the combined action of hydrogen and hydroxyl ions. In order to determine the quantity of acid in the exceedingly dilute solution (about 0·00005-normal), the conductivity, as being the best quantitative method, was employed.

The general result of the investigation has been the experimental confirmation of the theoretically predicted presence of a minimum in the velocity. What takes place here? The H- and OH-ions in the water cause the saponification; the acid which is formed undergoes electrolytic dissociation with the production of H-ions.

The equilibrium

$$\overset{+}{H} + \overset{-}{OH} \rightleftarrows H_2O,$$
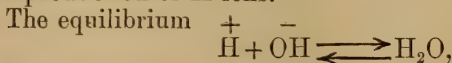
which takes place between the H- and OH-ions on the one hand and the water on the other, necessitates a diminution in the number of hydroxyl ions on the appearance of new hydrogen ions. The hydroxyl ions, however, saponify very rapidly, and from the velocity of saponification by bases it is calculated that they saponify 1400 times more rapidly than hydrogen ions. Hence there must be a decrease in the velocity caused by the disappearance of OH-ions, followed by an increase in the velocity due to the increased production of H-ions; in other words, there must be a minimum velocity.

If C represents the concentration of the ester, and C_H and C_{OH} the concentrations of the ions, we have mathematically:—

$$Velocity = KC(C_H + 1400\, C_{OH})$$

and

$$C_H C_{OH} = k.$$

The change of velocity is

$$dC_H + 1400\, d\, C_{OH},$$

the minimum velocity

$$d\, C_H = -1400 d\, C_{OH}$$

and

$$C_{OH} dC_H = -C_H dC_{OH};$$

hence

$$C_{OH} = \frac{C_H}{1400}.$$

The minimum therefore occurs when there are 1400 H-ions and one OH-ion present in the solution.

This is represented graphically in fig. 6. After about two hours the velocity sinks to about $\frac{1}{20}$ of its initial value. At this stage, two sets of experiments showed that a minimum actually existed.

A third experiment, performed with the greatest care, was therefore made in order to determine accurately the minimum velocity, and from this to calculate the electrolytic dissociation of water. The result which was obtained was 0.071×10^{-6} per

minute in a normal solution of ester, and the corresponding dissociation 0.12×10^{-6} of a gramme-molecule per litre.

Fig. 6.
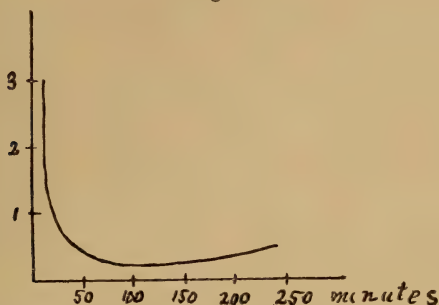
The great importance of this result is seen on comparison with the following numbers. Shortly before, Ostwald found in quite a different way that the electrolytic dissociation of water lay between 0.74×10^{-6} and 0.27×10^{-6} gram.-mol. per litre; whilst from Kohlrausch's conductivity determination he calculated that the maximum value did not exceed 0.6×10^{-6}. Arrhenius obtained 0.11×10^{-6} from Shields' experiments, and Bredig estimated it at about 0.6×10^{-6} gram.-mol. per litre.

Is the theory of electrolytic dissociation hereby proved? By no means. In the domain of saponification it has nevertheless accomplished far more than could have been expected.

XLVIII. *Note on the Elasticity of Spider Lines.*
By James H. Gray, *M.A.* (*Glas.*), *B.Sc.* (*Lond.*)*.

THESE tests were made last summer in the Physical Laboratory of Glasgow University, in the course of some work in which a very sensitive mirror-galvanometer was required.

When the mirror was suspended with a fine silk fibre, it was found that, when deflected, it took an inconveniently long time to return to zero. This defect, common to silk and most metal suspensions, and which has been called "creep," was, at the suggestion of Dr. J. T. Bottomley, F.R.S., obviated by using a spider's thread for supporting the mirror.

* Communicated by the Author.

In the Proceedings of the Royal Society for 1889, page 291*, an account is given of some very interesting tests made of the value of the torsional rigidity of spider's thread by Professor A. Tanakadate, of Japan. He found that the torsional rigidity is rather less than one sixth of that of silk fibre of the same thickness.

For the tests about to be described, several garden spiders, species *Epeira Diadema*, about one eighth of an inch in length of body, were caught and placed each in a separate box. Fresh threads, free from dust, could thus be obtained. If more than one spider was placed in the same box the number soon became reduced to one, the others having been killed and eaten by the survivor. It is necessary to employ the garden spider, as the house species, which makes a closely woven web quite different from the beautiful spiral of the *Diadema*, cannot be made to spin a thread. The spinner was taken out of its box and placed on a card or piece of wood held about three feet or so above the ground. A slight tap was sufficient to cause the spider to drop from the support, spinning a thread as it fell. Sometimes it dropped to the floor, but in most cases it stopped when it had fallen six or eight inches, and, after hanging apparently motionless for a second or two, rapidly threw out an exceedingly light thread which floated outwards and upwards in the direction of the slightest draught. In the space of ten seconds sometimes as many as ten feet of thread were thrown out. If the outer end of this thread happened to attach itself to one of the adjacent supports, the spider immediately endeavoured to make its escape. The threads thus spun were exceedingly thin, and could only be seen when a strong light was thrown upon them and with a black background.

While it was still floating, two marks were made about 50 centimetres apart, by carefully fixing with gum two pieces of the thread, each 3 millimetres long, at right angles to the length. Small wire weights from $\frac{1}{2}$ to 30 milligrammes were made, and half a milligramme was fixed a little beyond the furthest thread-mark. This was sufficient to bring the thread down to the vertical without appreciably stretching it. On a vertical stand were fixed two paper scales graduated in half-millimetre divisions, the one scale about 50 centimetres above the other. Directly in front of these scales the thread was hung, and by means of a telescope placed six feet away the readings corresponding to the two marks on the thread were obtained. Precautions were taken to prevent draughts, as

the slightest current was sufficient to drive the thread against the scales, from which it could only with difficulty be freed.

The small weights were gradually fixed to the lower end of the thread, and the corresponding readings of the marks taken. The data were thus obtained for a stress-strain diagram, and are shown on the annexed curve. The abscissæ represent percentage stretchings, and the ordinates weights applied.

The actual stretchings obtained are given below :—

Amount of stretching.	Percentage stretching.	Weight applied.
1·775 centim.	3·28	2·0 milligrammes.
2·775 ,,	5·11	3·5 ,,
4·25 ,,	7·85	6·5 ,,
5·1 ,,	9·42	8·5 ,,
6·325 ,,	11·68	11·5 ,,
7·175 ,,	13·25	13·5 ,,

Original length between the marks, 54·15 centimetres.

One milligramme corresponds to 127·3 kilogrammes per square centimetre.

The breaking-weight of this thread was found to be 17 milligrammes, that is, $2·16 \times 10^6$ grammes per square centimetre. This number does not differ greatly from those for the breaking-weights of copper (annealed), bronze, drawn gold, palladium, and silver. It is rather greater than that for cast iron, but considerably less than steel, and indeed than silk fibre.

The value for the breaking-weight per unit of cross section of the spider's thread is given on the assumption that the thread is circular. This is not quite correct, however, as it is really composed of four or six strands parallel to each other. Each of these strands, again, is made up of about one thousand exceedingly fine threads. The cross section of the complete thread being, therefore, virtually four or six small circles instead of one large circle, the value given above for the breaking-weight is probably from five to ten per cent. too small.

The diameter of the thread was very carefully measured for me by Dr. William Snodgrass, of the Physiological Laboratory, by means of a very finely-divided micrometer-scale and a powerful microscope. As measured by Dr. Snodgrass, the diameter was found to be almost exactly $\frac{1}{1000}$ of a millimetre.

One interesting point is at once apparent on looking at the form of the curve. Whereas in all metal threads, whenever

the elastic limit is exceeded, the extension increases in a greater proportion than the tension, in spider's thread, on the contrary, the extension at first increases more slowly than the tension, and afterwards goes on at exactly the same rate up to the breaking-point. It will be seen that the latter part of the curve is practically a straight line.

Stress-Strain Diagram of Spider's Thread.

Stretching-weight, in milligrammes. 1 milligramme corresponds to a stress of 127·3 kilogrammes per square centimetre.

Percentage Stretchings.
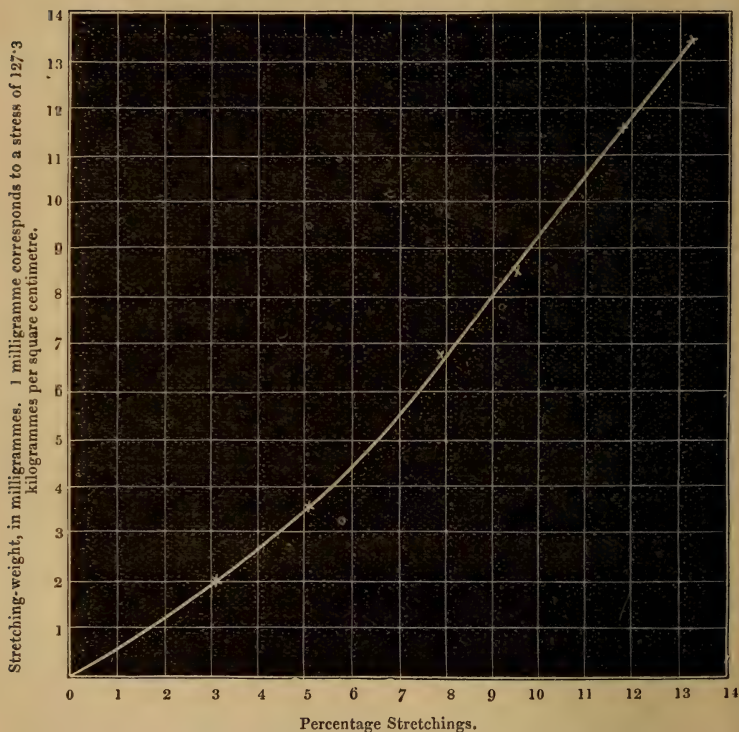
The behaviour of spiders' thread under stress is very similar to that of muscle and all animal tissue. They show a kind of tetanus tendency when stretched. It also resembles india-rubber, as shown in a stress-strain diagram obtained by Professor Archibald Barr in a testing-machine designed by him.

Subject to the error caused by want of circularity of the thread, the Young's modulus was found to be $7·769 \times 10^6$ grammes per square centimetre. This is much lower than the value for any metal, the lowest being that of lead, which

is 51×10^6, and even than any of the woods as given in volume iii. of Lord Kelvin's 'Collected Papers.' On account of the thread not being circular, the calculation of the Rigidity Modulus would of course be valueless.

A rough trial was made of the Torsional Rigidity; but as the thread was very much finer than that used by Professor Tanakadate, being about one third the diameter, it was difficult to obtain a light enough twisting-weight. The result obtained, however, agreed with that given by Prof. Tanakadate, in so far as it showed that the torsional rigidity of spiders' thread is considerably less than that of silk fibre.

XLIX. *The Method of Fractional Distillation illustrated by the Investigation of Kerosene. By* J. ALFRED WANKLYN *and* W. J. COOPER *.

A LIQUID known as kerosene, or Russian kerosene, is imported into this country in immense quantities. The liquid is produced by the distillation of crude natural Russian petroleum in Baku, and is conveyed in tank-ships to London. It arrives in this country in the condition of an almost colourless oil, with very little smell, and of sp. gr. 0·825 at 15°·5 C. Apparently it is very constant in quality and composition.

The knowledge of it which we owe to former investigators is that it is a mixture of hydrocarbons of the general formula C_nH_{2n}; that these hydrocarbons are not olefines, but are isomers of the olefines, being not readily attacked by reagents. Very few of the members of the series have been described by former investigators. We have made a study of kerosene as follows :—

When kerosene is rapidly distilled in a glass retort, 70 per cent. comes over below 250° C., about 20 per cent. between 250° and 300°, and the residual 10 per cent. may be almost completely volatilized; the last 5 per cent. requiring, however, a temperature much above the boiling-point of mercury.

By careful quantitative experiment, a carefully measured litre of kerosene being distilled in two operations, half a litre at a time, it was ascertained that there is neither expansion nor contraction during distillation. The observation was also made that not until the temperature had risen to 170° C. did the first drop of liquid distil over.

The actual figures of the experiment were as follows :—

		cub. centim.
Distillate between 170° and 250° . . .		688
,, ,, 250° and 300° . . .		205
Residue		107
		1000

That nothing should distil over below 170° is most remarkable, inasmuch as there is actually present in kerosene a liquid with a boiling-point of 78° C. The proportion of this low-boiling liquid is indeed small ; but there are other volatile ingredients, and the sum total of the ingredients boiling below 170° C. amounts to more than one fifth of the total kerosene.

The 688 cub. centim. of distillate (which has just been mentioned) were submitted to redistillation, and they yielded 505 cub. centim. below 210° C. And in that manner one litre of kerosene was caused to yield 505 cub. centim. of distillate below 210° C. When it is directly distilled a litre of kerosene does not give anything like half its volume of distillate at temperatures below 210° C.

Continuing the investigation, the 505 cub. centim. of distillate were redistilled, and they began to distil at 125° C., and up to 170° C. 270 cub. centim. came over. And in that manner a litre of kerosene (which when directly distilled yields only one drop of distillate below 170° C.) may be caused to evolve 270 cub. centim. of distillate below 170° C.

All this illustrates how admixture with a high-boiling liquid raises the boiling-point of low-boiling liquids.

We have carried out a most laborious investigation of kerosene, and, operating on a considerable scale, after many months of fractionation have separated 24 different liquids, which, with probably a few others, and together with about 13 per cent. of residue boiling at temperatures above 290° C., make up the complex mixture known as kerosene. As to the proportions of the different ingredients of the mixture, it is to be noted that there is no one preponderating ingredient. There appears to be a very small proportion of the two most volatile terms of the series, but for the rest the distribution is not very uneven. We doubt whether the proportion of any one ingredient exceeds 5 per cent. of the whole kerosene.

In the following table are set forth the main results of our work :—

Tabular statement of the Constituents of Kerosene.

| Label. | Boiling-point. | Vapour-density. | | Formula. |
		Found.	Theory.	
A	77° C.			
Az........	87			
Aa.........	96·5	3·69	3·63	$C_{7\frac{1}{2}} H_{15}$
Ab........	106	3·91	3·87	$C_8 H_{16}$
B	116·5	4·08	4·11	$C_{8\frac{1}{2}} H_{17}$
Bb........	127	4·36	4·35	$C_9 H_{18}$
Bc	138	4·59	4·59	$C_{9\frac{1}{2}} H_{19}$
C	148	4·84	4·84	$C_{10} H_{20}$
D	158	5·02	5·08	$C_{10\frac{1}{2}} H_{21}$
Dd........	168	5·20	5·32	$C_{11} H_{22}$
De	176	5·51	5·56	$C_{11\frac{1}{2}} H_{23}$
E	186	5·77	5·80	$C_{12} H_{24}$
F	197	6·08	6·04	$C_{12\frac{1}{2}} H_{25}$
Ff	205	....	6·28	$C_{13} H_{26}$
G	214	6·53	6·52	$C_{13\frac{1}{2}} H_{27}$
Gg	222	6·83	6·77	$C_{14} H_{28}$
H	230			
Hh........	237			
I	246			
K	253			
L	260			
M	267			
N	274			
O	280			

Z Residue—a dark coloured liquid (sp. gr. about 0·880 at 15°·5 C.), being a mixture of several liquids of very high boiling-point.

The series of liquids, A to O, presents the following characters. Each liquid, when distilled separately in the well-known fractionation-flask, begins to distil about 10 degrees higher than its predecessor begins to distil. Thus the first term A begins to distil at 77°·5 ; the second term Az at 87° ; the third term Aa at 96° ; the fourth term Ab at 105°·5 ; the fifth term B at 116° ; the sixth term Bb at 127° ; the seventh term Bc at 138°, and so on up to the last term O.

Except the few highest terms the members of the series fulfil the requirement, viz. that half of the liquid shall distil without the thermometer rising more than 2 or 3 degrees, that three-quarters shall distil within 5 or 6 degrees of the starting-point, and that by the time the boiling-point of the next in the series is reached 90 per cent. shall have distilled over.

Within the last few weeks the seven lowest terms, viz. A

to Bc inclusive, have been prepared anew from fresh kerosene and fractionated with great perseverance. The first two terms A and Az have not yet been procured in sufficient quantity to admit of the very elaborate treatment to which we should like to subject them, but the five next terms, Aa to Bc inclusive, have been obtained in abundance and have been exhaustively treated.

As an example we will quote the record of the final testings of Aa :—

Exp. I.—Vol. of Aa employed = 136 cub. centim.

°C.

At 96·2 . . . 5 cub. centim. had distilled.

97·2 . . . 50 ,, ,,

98 . . . 75 ,, ,,

99·2 . . . 100 ,, ,,

105 . . . retort dry.

Exp. II.—Vol. of Aa, 132 cub. centim.

°C.

96 . . . 5 cub. centim. had distilled.

97 . . . 50 ,, ,,

99 . . . 100 ,, ,,

105 . . . dry.

Exp. III.—Vol. of Aa, 130 cub. centim.

°C.

95·8 . . . 5 cub. centim. had distilled.

96·8 . . . 50 ,, ,,

98·8 . . . 100 ,, ,,

104 . . . dry.

Showing that three-quarters of Aa distils over without a greater rise than 3 degrees, and that the retort becomes dry before the boiling-point of Ab is reached.

Before making the three final distillations Aa had been deprived of traces of Az (the next lower term) by the following course of procedure.

139 cub. centim. of Aa was placed in a retort and 50 cub. centim. was then distilled off. Next the 50 cub. centim. of distillate was redistilled thus :—

94°·8 C. . . 5 cub. centim.

96 . . 16 ,,

Then the 16 cub. centim. of distillate was redistilled,

94° . . 5 cub. centim.

and 8 cub. centim. was distilled off and rejected.

As has been said, five consecutive terms, viz. Aa, Ab, B, Bb, and Bc, have been exhaustively treated, and each one has been proved to be incapable of being resolved into fractions with different boiling-points. We believe that the conclusion cannot be resisted that the kerosene series of hydrocarbons mounts by increments of 7 instead of by increments of 14, and we hold that the real atomic weight of carbon is 6 and not 12.

Laboratory, New Malden, Surrey,
     14th April, 1894.

L. *Notices respecting New Books.*

UNIPLANAR ALGEBRA : *being* Part I. *of a Propædeutic to the Higher Mathematical Analysis.* By IRVING STRINGHAM, *Ph.D., Professor of Mathematics in the University of California.* San Francisco, the University Press.

"THE logical grounding of Algebra," writes the author in his preface, " may be essentially arithmetical or geometrical. I have chosen the geometrical form of presentation and development." "The point of departure is Euclid's doctrine of proportion, the fundamental propositions of which are enunciated and proved in an Introduction (pp. 1–20) in which I have followed the method recommended by the Association for the Improvement of Geometrical Teaching."

With Chap. I. commences the explanation of the "Laws of Algebraic Operation" as affecting real, or magnitudes involving only the idea of length ; imaginary, including also the idea of turning through a right angle, and complex, embodying length and rotation through *any* angle. The product is obtained as a fourth proportional to the unit, or "*idemfactor*" (Peirce), and the factors of that product ; the quotient as a fourth proportional to the unit, the dividend, and the reciprocal of the divisor. Indeterminate Forms are here introduced, their evaluation being treated of lower down ; combinations of signs, the Associative, Commutative, and Distributive Laws are successively treated of and proved. Logarithms are defined in Napier's manner, treated so as to introduce the conceptions of the modulus and base as well as exponential, whose Laws—of Involution and the Index—are proved. The law of the interchange of indices and coefficients in Log Operations is called by the distinct name "Metathesis." To conclude the chapter, Indeterminate Exponential forms are touched on, and a useful synopsis of the matter of the chapter added.

Chap. II. contains an introduction to the circular hyperbolic and Gudermannian functions, with proofs of some fundamental limits.

Chap. III. is occupied with "Complex Quantities," represented

by vectors, of which real quantities represented by segments of the axis and " imaginary " by vectors perpendicular to that line are particular cases. Perhaps more unity would have been imparted to the terminology by the substitution of " unreal " for " imaginary;" then " real " would have expressed the complex of which the component perpendicular to the axis vanishes ; " unreal," that the real component of which is zero. The abbreviation cis. θ, to be read *sector of* θ, is adopted for the complex $\cos\theta + i\sin\theta$. The associative, commutative, and distributive laws are then proved for complex magnitudes. All this has, of course, been founded on Argand's construction, which, however, is only formally explained hereafter.

In the second section of this Chap. III. the Exponentials and Logarithms of complex quantities are dealt with by means of a diagram ; the theory as adopted having been the subject-matter of a paper by the author read before the New York Mathematical Society in October 1891, and subsequently published in vol. xiv. of the Am. Journ. of Math. Without the diagram, a description of this theory would be hardly intelligible. Just as the vanishing of an angle causes the complex to degenerate into a real, so in the diagram referred to the vanishing of an arbitrary angle in it changes the Exponentials and Logarithms of complex into those of ordinary magnitudes. The result of these discussions leads to the definition of " an Algebra ;" viz. since the aggregate of all complexes operating howsoever on one another form a " closed group," *i. e.* evolve only complexes, such a group forms an Algebra. Reference is made to Peirce and Cayley.

The chapter concludes with proofs that every magnitude can be expressed, with an error less than any assignable, in terms of an assumed unit by a rational number.

Chap. IV. treats of the Cyclic and Hyperbolic Functions (direct and inverse) of complexes, defined with respect to a complex modulus (κ), and hence called " modo-cyclic " functions, having a period $2i\kappa\pi$ or $i\kappa\pi$, and of the inverses of these.

Chap. V. explains the one to one correspondence of points on a plane and on a sphere, having its centre in the plane, through rays drawn from one end of the normal diameter, and the transformation of the planar complex into the tri-dimensional sphero-surface complex (Cayley, Klein). The rest of this chapter on " Graphical Transformation " is occupied with some particular cases of " Orthomorphosis " (Cayley). In it occurs the only misprint which has been noticed, of a symbol B^w for B^{w_0}. The typography is highly creditable to the San Francisco press—is, in fact, dainty of its kind.

In the concluding chapter, " Properties of Polynomials " with complex coefficients are proved, after a preliminary page on the evaluation of the n–nth roots of a complex quantity ; this, as every other branch of the matter of the book, being illustrated by a collection of " Agenda " or Examples, on which the student may exercise himself.

So much must suffice to give an idea of the object and scope of this small volume, which, it should be said, presupposes " a familiarity with the elements of algebra and trigonometry." To students thus qualified "its subject-matter and treatment constitute a rapid review of the underlying principles of those subjects, including in its most general aspects the algebra of complex quantities."

<div style="text-align: right">J. J. W.</div>

Elasticity. By Dr. B. WILLIAMSON, *F.R.S.*
(London : Longmans, 1894 ; pp. x + 135.)

THE full title, viz. 'Introduction to the Mathematical Theory of the Stress and Strain of Elastic Solids,' indicates that this little book is an elementary one, and that it does not treat of the more advanced portions of the general Mathematical theory. These, as our readers know, are admirably discussed in Mr. Love's fuller treatise. The subject is of the highest practical importance, and we are glad to have such an Introduction drawn up by so competent a writer as Dr. Williamson. Our author states at the outset that he adopts the notation suggested years ago by the late Professor Townsend : a notation which " has the advantage of harmonizing with the generally recognized method of representing the equation of a surface of the second degree." The discussion is in the main confined to the consideration of perfectly elastic solids, so that the results are, of course, only approximately true for actual substances.

The work is divided into five chapters. In Chapter I., *Strain* is treated of under the heads of Homogeneous and Heterogeneous Strain, and Strain in Curvilinear Coordinates. Chapter II. is devoted to Homogeneous and Heterogeneous Stress. The connexion between Stress and Strain is the subject of Chapter III., and occupies three sections, on Work and Potential Energy, Case of Isotropic Substances, and Applications. The Torsion of Prisms is considered in Chapter IV., and Elastic Beams in Chapter V. From this summary it will be seen that a fair amount of interesting ground is covered. That the text is clearly put goes without saying, but there is no great scope for novelty of treatment. Dr. Williamson takes care to give references, where called for, to recent memoirs and treatises bearing on the subject. It only remains to add that each chapter is closed with a selection of good illustrative exercises from College Problem papers, and that there is an index at the close of the volume.

On the Definitions of the Trigonometric Functions. By A. MAC-FARLANE, *D.Sc.* (Boston : J. S. Cushing & Co. ; 49 pp.)

THIS is a paper the substance of which was communicated to the Mathematical Congress at Chicago on the 22nd August in last year. It is a following up of previous papers by the same author on points connected with Space Analysis. Three of these are respectively entitled ' Principles of the Algebra of Physics,' in which Dr. Macfarlane introduced a certain trigonometric notation

for the partial products of two vectors. This notation has been discussed by Mr. Heaviside in the ' Electrician ' (December 9th, 1892), by Prof. Alfred Lodge in ' Nature ' (November 3rd, 1892) and elsewhere. The present paper is in part a rejoinder to the statements of these gentlemen. Then followed a paper on ' The Imaginary of Algebra,' and ' The Fundamental Theorems of Analysis Generalized for Space.'

The author here proposes " to review critically the historical definitions of the trigonometric terms, and the definitions, triangular, circular, or hyperbolic, given in the best modern treatises at my command ; then to devise a logical system of definitions which will apply to space-analysis and that modern trigonometry, which, as Prof. Greenhill shows (Diff. and Int. Calc. p. 61), includes the properties both of circular and hyperbolic functions, and will be able to bring within the same domain the properties of the elliptic, general hyperbolic, and other functions."

This wide extent is not gone over here, but attention is mainly given to Plane Trigonometry : Trigonometry in space is handled in a further pamphlet entitled ' The Principles of Elliptic and Hyperbolic Analysis.'

Dr. Macfarlane discusses in detail the treatment adopted by De Morgan and more recently by Dr. Hobson, Messrs. Levett and Davison, and Mr. Hayward (in his ' Vector Algebra and Trigonometry '). M. Laisant's *Essai sur les fonctions hyperboliques* is noted with warm approval, and then Dr. Macfarlane proceeds to show how the " several species of trigonometric functions—the triangular, the circular, and the ex-circular " (using Mr. Hayward's nomenclature) " may be defined in harmony with one another. The method adopted is afterwards shown to be applicable to the logarithmic spiral, ellipse, and general hyperbola, and to a mixed curve composed partly of a circle, partly of an ex-circle." In the pamphlet which follows the one before us the method is said to be applied to ellipsoidal and hyperboloidal trigonometry.

To the Editors of the Philosophical Magazine.

Gentlemen,

Will you kindly allow me to offer a word of explanation respecting the notice of Wiedemann and Ebert's ' Practical Physics,' which appeared in the March number of the Philosophical Magazine (p. 334). In writing the notice I had occasion to refer to the treatise by Prof. F. Kohlrausch as seeming "somewhat antiquated in a modern laboratory." It should be stated, in justice to Prof. Kohlrausch, that this remark was intended to be applied only to the earlier editions of his work ; in a recently published German edition the text has been revised and many new experiments have been added. A similar revision of the English translation is greatly to be desired.

<div align="right">I remain, Gentlemen,
Yours truly,</div>

University College, Liverpool,
April 16th.

<div align="right">JAMES L. HOWARD.</div>

LI. *Intelligence and Miscellaneous Articles.*

ON THE THERMAL BEHAVIOUR OF LIQUIDS.

To the Editors of the Philosophical Magazine.

GENTLEMEN,

IN answer to the letters of Drs. B. Galitzine and P. de Heen in the April number of this Journal, we beg to make the following remarks :—

It is quite true, as stated by Dr. Galitzine, that our criticism of the arrangements employed to obtain constant high temperatures does not apply to him (provided that the naphthaline employed by him as a jacketing vapour was pure). This, however, we pointed out in our paper, at the same time calling attention to the fact that the method was, with certain modifications, that employed and recommended for many years by ourselves. We think, however, that Dr. Galitzine's results are open to criticism on the following grounds :—(1) The complete elimination of alcohol from ether is not an easy matter, and cannot be effected by the action of metallic sodium ; but no other method of purification is mentioned in his paper. The last trace of alcohol may be removed by shaking the ether twenty or thirty times with small quantities of water, or by repeated distillation over phosphorus pentoxide ; but we do not know of any other method. (2) Although we fully appreciate the great pains taken by Dr. Galitzine to purify his ether from air, yet we doubt whether any method involving the sealing of a glass tube is capable of giving perfectly satisfactory results. In the Trans. Chem. Soc. for 1891, p. 37, a new method of determining the specific volumes of liquids and of their saturated vapours was described by one of us ; and experience has shown that the chief difficulty in this method is the necessity of sealing the tube containing the liquid. The vapour of the liquid may undergo slight decomposition owing to the high temperature, or a trace of air may be expelled from the glass. It has been frequently observed in the experiments carried out by this method that when a minute quantity of air or permanent gas is present, the attainment of the final state of equilibrium is greatly retarded. It has also been observed that the retardation increases with the amount of permanent gas present, and that if there is a comparatively large amount (though actually a very small one), the results are rendered entirely untrustworthy.

The influence of the permanent gas has also been found to increase rapidly as the critical point is approached, though it may be very marked at much lower temperatures. This question has been shortly discussed by one of us (Trans. Chem. Soc. 1891, p. 128), and very fully by Dr. J. P. Kuenen (*Verslagen der Afdeeling Naturkunde der Kon. Akademie*, Leiden, April 1892, p. 422 ; June 1892, p. 15 ; Oct. 1893, p. 85) ; and we fully agree with Dr. Kuenen in the great importance he attaches to retardation.

Dr. de Heen requests us to point out the errors of reasoning or experimentation that he has made in the demonstration of his fundamental proposition, and asks for an explanation why we characterize his paper as " very inaccurate."

Our criticism, which refers to the experimental work on which the reasoning is based, was caused by the very wide discrepancies between the critical temperatures observed by Dr. de Heen and by other experimenters. As examples we may cite the following :—

Substance.	Critical temperature.	Observer.
Methyl formate, A*	214·0° C.	Young & Thomas.
B	214·0	
	212·0	Nadejdine.
	250·5	De Heen.
Methyl acetate, A*	233·7	Young & Thomas.
B	233·7	
	232·9	Nadejdine.
	229·8	Sajotschewski.
	239·8	Pawlewski.
	278·7	De Heen.

With such differences in the most easily determined critical constant it seemed to us to be useless to discuss the much more difficult observations on volumes.

We are still of opinion that the interpretation of M. Gouy may be admitted, and we think, with Dr. Kuenen, that the reason why a stable equipoise in a vertical tube is not immediately produced is due to the presence of impurity, in most cases of air or other permanent gas.

W. RAMSAY.
S. YOUNG.

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SUPPLEMENTARY REMARKS ON CHANGES OF TEMPERATURE CAUSED BY CONTACT OF LIQUIDS WITH SILICA†. BY DR. G. GORE, F.R.S.

In addition to the remarks already made on the results of the experiments in the above research, I beg leave to offer a further explanation of the phenomena, and to say that all such changes of temperature caused by the mere contact of liquids with solids are, in my opinion, consistent with the statement that *whenever two substances approach or touch each other, they lose energy* ; and when they mutually recede, the opposite effect occurs.

That this statement appears to be true of all bodies, whether they are similar or dissimilar, of atoms, molecules, and masses, is shown in many ways, only a few of which need be mentioned. It is shown as loss of potential mechanical energy by falling bodies,

* The letters A and B refer to two different specimens.
† See Philosophical Magazine, March 1894, pp. 306–316.

usually as loss of heat when substances of any kind are compressed, when liquids "adhere" to solids (as in the above experiments), and when substances chemically "combine;" it is also shown, though in a less simple form, when bodies approach each other by electric and magnetic "attraction." Conversely, when a gas is rarefied by mechanical means, it gains heat by absorption; similarly, when a film of air adhering to a solid is displaced by a liquid, and when the molecules of a solid or a liquid are separated farther asunder by a solution in a liquid without chemical union, or by dilution of its solution, heat is usually absorbed.

Although in every one of the 98 experiments of the above research heat was evolved and lost, in about half of the 58 trials with silica the dissolved substance appeared to *absorb* heat by contact with the powder. These apparent exceptions were probably due to the amount of heat absorbed by the receding film of air being greater than that evolved by the approach and contact of the dissolved substances, and thus those cases were made to appear inconsistent with the above general statement. Similarly, instances of electric and magnetic "*repulsion*" are probably only apparent exceptions to that statement, the real phenomena being obscured by the attendant circumstances.

As in all these various cases, whether of "adhesion" of films of air, water, or dissolved substance to solids, of chemical union, or of electric and magnetic attraction, the only factors of the mechanical energy of the molecules are *mass* and *velocity*, and as in every instance the mass of neither of the acting substances is perceptibly altered, the loss of mechanical energy of bodies by mutual approach and contact, and the gain by mutual recession, must consist entirely of *velocity*. It is well known that a solid when dissolved in a liquid behaves like a gas, and as the molecules of a gas "move faster the better the exhaustion" (Crookes, Phil. Trans. Roy. Soc. 1879, p. 160), so do those of a liquid by being separated by dilution; this increase of molecular velocity by dilution is also shown by an increase of electromotive force (see Proc. Birm. Phil. Soc. vol. viii. pp. 63–138).

As these supplementary remarks appear to afford a much wider and more complete theoretical explanation of the phenomena observed with silica &c. than that offered in the original communication, I venture to submit them for consideration.

POLARIZATION OF NON-DIFFRACTED INFRA-RED RADIATION BY WIRE GRATINGS. BY H. DU BOIS AND H. RUBENS.

The results of this investigation, a preliminary account of which was given at the Edinburgh B. A. Meeting (1892), may be summarized as follows:—

Gratings were finally made of metal wire down to a diameter of 2·5 mcm. ("millicentimetre" = 0·001 cm.), the interspaces between

the wires being equal to their diameter; by inclining the grating relatively to the wave-front, the apparent clear spaces available for the passage of radiation could be reduced to 1 mcm. The wavelengths investigated ranged from about $\frac{2}{3}$ of the above unit down to that of red light. The method employed was a somewhat elaborate spectrobolometric one; it was exclusively applied to the non-diffracted part of the incident radiation, corresponding to the so-called " central image."

It was found that all wire gratings polarize perpendicularly to the direction of the wire so long as the wave-length is very small; for larger wave-lengths the action is, however, reversed. The intermediate value of the wave-length, at which the grating does not polarize, *i. e.* the " neutral point," is independent of the geometrical constants of the grating, but characteristic for the metals constituting its wires. Its value increases in the order Pt, Ag, Au, Fe, Cu. The wire gratings behave like polarizers in every respect. Malus' law, properly modified, was found to hold for the polarizing action in different azimuths. The polarizing action increases as the apparent clear space diminishes: the ratio of the intensities of the two perpendicular components of radiation, which measures that action, could be pushed up to over 2. The results were checked by a simpler method of a more qualitative character, which may prove useful for a repetition or demonstration of the experiments.

The authors then give a general discussion of the phenomenon, its possible relations to other phenomena, the influence of diffraction, and, lastly, the possible explanation by it of the properties of æolotropic dielectrics. This particular part of the paper presents certain analogies with Lord Rayleigh's theoretical discussion of " the influence of obstacles arranged in rectangular order upon the properties of a medium " (Phil. Mag. Dec. 1892).

However, the principal interest attaches to the experiments described, when viewed in the light of the electric theory of radiation and of Hertz's discoveries: the diminutive polarizing gratings in the present case being quite analogous to the large electromagnetic wave-polarizers first introduced by that great investigator.

Since there can hardly remain a doubt that in the electromagnetic theory, the electric vector must be considered perpendicular to the plane of polarization, the magnetic vector parallel to it (Trouton, Klemenčič, Righi), the action of polarizing gratings in general may now be described as follows:—

As long as the wave-length keeps below a certain value characteristic of the metal, the grating allows the greater fraction of incident radiation to pass in case the electric vector be parallel to the wires; whereas for longer waves the transparency is greater if the magnetic vector have that direction. For further particulars the original may be referred to.—Wiedemann's *Annalen*, xlix. p. 593 (1893).

MAGNETIZATION OF HOLLOW AND SOLID CYLINDRICAL CORES.
BY H. DU BOIS.

The vexed question of hollow *v.* solid cores is once more discussed in this note. Von Feilitzsch's well-known result that the magnetic moment of short hollow cores is hardly inferior to that of solid ones (other circumstances equal and saturation not being approached) has been elegantly explained by Prof. Silv. Thompson in a general qualitative way by the simple remark that the external air-resistance is approximately the same in both cases. There is no need whatever, therefore, for the assumption that the central fibres of cores are less easily " reached " by temporary steady magnetization than those near the skin: such a state of things would only be proved if the same result were obtained with hollow endless rings, which is improbable.

Von Feilitzsch's experiments having been lately repeated and extended by Prof. Grotrian (Wied. *Ann.* l. p. 705, 1893), the author seized the occasion for attempting to go into the matter somewhat more fully. The particular case of a cylinder being one of those in which the modern " magnetic circuit " notion does not lead up to quantitative results so well as the more orthodox theory of induction, the latter had to be applied, and immediately yielded the following general rule :—

If for cylindric or prismatic bodies of given length and any shape of section the " demagnetizing factor " be proportional to the latter and not too small, then the magnetic moment will be practically independent of the section for fields which are not so strong as to produce an approach towards saturation.

It is further shown that both premises of this rule apply to thin hollow cores, for which it is thereby easy to draw the curves of magnetic moment and impressed field up to thorough saturation for any given dimensions. An illustrative diagram of such curves is given, which presents exactly the same aspect as the experimental diagram of Prof. Grotrian's paper. Finally, the question of hollow cores for dynamos is touched upon. Signor Ascoli has since independently criticised Prof. Grotrian's results much on the same lines.—Wiedemann's *Annalen,* li. p. 529 (1894).

MOLECULAR ENERGY OF GASES. A CORRECTION.

On page 420, line 9, the word " every " is wrong. It is only because collisions are occurring in every direction that *on the average* the original difference of energy diminishes with each collision.—O. J. L.

ON A FUNDAMENTAL QUESTION IN ELECTRO-OPTICS.

To the Editors of the Philosophical Magazine.

GENTLEMEN,

In the April number of the Philosophical Magazine Dr. Kerr has published a paper, "Experiments on a Fundamental Question in Electro-Optics." Dr. Kerr finds the velocity of light changed by electric stress in electrostatically strained liquids only for light polarized perpendicular to the lines of force.

My paper on the same subject is not mentioned in which, eleven years ago, I treated this question with the identical methods employed by Dr. Kerr. (*Cf.* G. Quincke, "Electrische Untersuchungen, IX. Ueber die Aenderung der Brechungsexponenten von Flüssigkeiten durch electrische Kräfte," Wiedemann's *Annalen*, xix. pp. 773–782, 1883.) A proof of this paper I sent immediately after its publication to Dr. Kerr, who first observed the double refraction of light by electric stress.

But the results of my experiments were different from those of Dr. Kerr. I observed sometimes an increase, sometimes a diminution, of the velocity of light whose plane of polarization is parallel to the lines of force. I supposed that the reason of this ambiguous change were two forces of opposite character, *i. e.* the heating of the liquid by vortex motion and the electric pressure, both excited at the same time by the electric forces.

Heidelberg, Physical Laboratory of the   G. QUINCKE.
        University, April 21, 1894.

MOLECULAR ENERGY OF GASES.

To the Editors of the Philosophical Magazine.

GENTLEMEN,

With reference to the remarks made by Professor Lodge in the Philosophical Magazine for April, page 419, I only need to notice the chief point and to say :—It appears to me that the proposition that the amounts of mechanical energy of the molecules of different gases are equal, is of so fundamental a character that it ought, for the advancement of science, not to be limited to algebraic expressions readable only by mathematicians, but it should, *in addition*, be explicitly expressed in simple words (as Avogadro's law usually is) in every text-book of physics and monograph on gases, for the benefit of all persons.

I beg to remain, Gentlemen,
Yours truly,
Birmingham, April 6, 1894.   GEORGE GORE.

P.S. Had the "statement" I asked for in my previous letter (*not an algebraic expression*) existed in any of the text-books of science I should almost certainly have seen it, and that letter would not have been necessary.

LII. *On Interference Phenomena.*
By ARTHUR SCHUSTER, *F.R.S.*[*]

1. GOUY [†] and RAYLEIGH [‡] have recently discussed the question of interference phenomena observed with a source of white light, and have arrived at important results. When the two interfering beams pass through the slit of a spectroscope, the spectrum is seen to be crossed alternately by bright and dark bands, and if high resolving powers are used, these interference effects may be observed, although the difference of path of the two original beams is considerable. This well-known fact has always been taken to prove that the vibrations of the white light are to a certain extent "regular," and efforts have been made to find by experiment the limits of that regularity. The futility of these efforts has been completely demonstrated by Gouy and Rayleigh, who have proved that the bright and dark bands alluded to would appear with sufficient resolving power, even if light consisted of perfectly irregularly distributed instantaneous impulses. These investigations would seem, therefore, to lead to the conclusion that a source of light is completely defined by the distribution of energy in the

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[*] Communicated by the Author.
[†] Gouy, *Journal de Physique*, (2) v. 1886.
[‡] Rayleigh, *Encyclopædia Britannica*, "Wave-theory," § 7; Phil. Mag. xxvii. p. 463 (1889).

spectrum, and that there is no room for any such property as "regularity" independently from that implied in the connexion between energy and wave-length. A spectrum which possesses the same energy for all wave-lengths would prove complete irregularity of the source, while one in which the energy vanishes except for one definite wave-length would be due to a completely regular source. I confess that on first reading through the investigations which I have quoted, some difficulties presented themselves which it seemed necessary to clear up before these conclusions could be accepted in their full generality. There could be no doubt that Gouy's and Rayleigh's results were correct in the case specially examined by them, in which the analysing spectroscope has a resolving power which is gradually increased; but if we go to the other limit and gradually diminish the resolving power, would it necessarily follow that all sources of white light behave in the same way, and that the bright and dark bands would in every case disappear at the same time, the difference of path being kept constant? A test case (7) occurred to me, which seemed to leave a loophole through which we might still save some of our inherited notions about "regularity" of vibration. Although further investigation proved that the difficulties were only imaginary, and that we must accept the new views without restriction, I think that the importance of the subject deserves a more detailed treatment than has yet been given to it.

In order to put the question at issue as clearly as possible, it is necessary shortly to allude to the history of the subject.

2. The fact that rays of light emanating from two different sources do not produce so-called interference phenomena is fundamental, and was always recognized as such. It naturally suggested the idea that the vibrations of luminous particles are frequently disturbed, and this, again, led to the further conclusion that interference between rays emanating from the same source should cease if the difference in path were sufficiently increased. Fresnel looked on each particle of matter as vibrating during a certain time according to the simple pendulum law, and considered the group of waves sent out by the particle. If the group is divided into two, one being retarded as compared with the other, "interference" will take place. If the difference in path is equal or greater than the length of the group, Fresnel argued that interference should cease. "But," he adds, "another cause much sooner prevents our observing the mutual interference of two systems of waves, when the difference of path is somewhat great: it is the impossibility of rendering light sufficiently homo-

geneous." Here follows the well-known argument as to the effects of want of homogeneousness in the interfering rays.

Foucault and Fizeau * more definitely put it as a question for experimental determination, whether interference phenomena are ultimately stopped by want of homogeneousness or want of " regularity." Experimenting with white light, they came to the conclusion that their experiments " reveal in the emission of successive waves a persistent regularity which no phenomenon has hitherto suggested."

The opinion put forward by Fizeau and Foucault that observations on interference of light with large difference of path could teach us something as to the " regularity " of the vibrations of a particle was generally accepted, until more closely examined by Gouy and Rayleigh in the papers already alluded to. Their conclusions did not, however, receive the attention they deserve. Thus, in the last part of the *Encyclopædia der Naturwissenschaften*, it is stated that " if natural light really consists in a succession of different states of vibration, these take place so slowly, that in a time which is greater than 50,000 period, light must still be considered as essentially of the same type of vibration."

3. Compare with this the following passage taken out of Gouy's paper :—

" Ainsi l'existence de franges d'interférences à grande différence de marche, dans le cas des sources de spectres continus et de la lumière blanche n'implique nullement la régularité du mouvement lumineux incident. Cette regularité existe dans le spectre, mais c'est l'appareil spectral qui la produit, en séparant plus ou moins complètement les divers mouvements simples, qui jusque là n'avaient qu'une existence purement analytique."

Lord Rayleigh, in his article on the " Wave Theory," expresses the same idea as follows:—

" Or, following Foucault and Fizeau, we may allow the white light to pass, and subsequently analyse the mixture transmitted by a narrow slit in the screen upon which the interference bands are thrown. In the latter case we observe a channelled spectrum, with maxima of brightness corresponding to the wave-lengths $bu/(n\mathrm{D})$. In either case the number of bands observable is limited solely by the resolving power of the spectroscope, and proves nothing with respect to the regularity or otherwise of the vibrations of the original light."

Put shortly, the argument in favour of the above view is this :—Any disturbance, however irregular, may by Fourier's

* *Académie des Sciences,* 24th Nov. 1845 and 9th March 1846.

theorem be resolved into a series of disturbances each of which corresponds to homogeneous light. It is the object of a spectroscope to separate laterally these homogeneous vibrations, and no matter what the nature of the original light, the greater the resolving power of the spectroscope, the more nearly will it give us homogeneous light.

4. The argument is at once seen to be conclusive in one direction. However irregular the original light, interference bands with large difference of path may always be produced, if a spectroscope of sufficiently high resolving power is used. But there is another side to the question. In order that Fourier's series should correctly represent a given disturbance, there must be a definite phase relation between the different terms of the series. If a spectroscope of small resolving power is used, and if it is required to calculate the disturbance at the focus, we are not allowed to consider the different components of Fourier's series as independent, but must take account of this relation of phase. An example will show that in special cases altogether incorrect results will be obtained if this is neglected. Thus, let the light falling on the slit of a spectroscope be screened off until a given time, when the screen is removed but replaced subsequently after a short interval. The disturbance may by Fourier's series be decomposed into a series of simple * vibrations lasting through an infinity of time ; and if each component could be treated independently of another, it would follow that an eye examining the spectrum would continue to see light for any length of time after the incident beam has been cut off. This of course is absurd. The analysis by Fourier's series leads to results which are perfectly correct, if, when finite resolving powers are used, we take account of the phase relations between the component vibrations.

It seems therefore advisable to consider the effects of finite resolving powers a little more in detail, although it will appear that even then the effects produced can give us no

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* Is it too late to abolish the term "harmonic" vibration to express the projection of a uniform circular motion? The term "harmonic" seems to me to imply a relation between two things, and is very useful when we want to distinguish between, say, harmonic and inharmonic overtones. It is quite correct to speak of the expansion in a Fourier's series as an harmonic expansion, because the different terms are harmonically related, but each of them taken separately is not harmonic. Much confusion has been caused by a series of lines in a spectrum being called harmonics, because their distribution suggested some definite connexion between their periods, independently of the question whether that connexion was of the harmonic character. The term "simple" vibration seems to me to be well adapted to express a sine vibration.

information concerning "regularity" of vibration. But in the first place we must ask ourselves whether we can attach any meaning to the expression "regularity" of vibration when applied to white light.

5. To quote Lord Rayleigh once more:—" It would be instructive if some one of the contrary opinion would explain what he means by regular white light. The phrase certainly appears to me to be without meaning—what Clifford would have called *nonsense*" *.

I believe that those who speak of the regularity of vibration in a continuous spectrum have in their mind the state of motion of the original vibrating system, and not that of the medium through which the light is transmitted. If we imagine the light to be produced by a number of different vibrating systems, each sending out homogeneous vibrations, prismatic decomposition would give what we should call a line spectrum. We may imagine the lines of the spectrum to be so close together that any resolving power which we can apply fails to separate them.

There is nothing to prevent our imagining for the sake of argument that all continuous spectra if examined by resolving powers, say a million times larger than we can apply at present, would ultimately appear to be line spectra, each line representing perfectly homogeneous light; and if each line is due to a separate vibrating system, we may reasonably say that that system remains perfectly regular for an indefinite time. Let us then imagine a practically continuous spectrum of this nature in which, for the sake of simplicity, there is no difference in intensity, all wave-lengths being equally represented. The spectrum might be made completely continuous by imagining each vibrating system to be split up into several, moving with uniform velocities in different directions, and that velocity may be made indefinitely small, as the difference in wave-length between the vibrating systems is indefinitely reduced. But for my purpose it will be sufficient to take the spectrum as ultimately discontinuous, and I shall take such a system of vibrations as the representative of what may be called "regular" white light. On the other hand, imagine a set of molecules setting up a luminous disturbance by perfectly irregular and indefinitely short impulses. When examined by a spectroscope we should see a continuous spectrum ranging over all wave-lengths with equal intensities; of such we may imagine "irregular" white light to consist.

The question I shall discuss in detail is this :—Can we by

* Phil. Mag. xxvii. p. 463, note (1889).

any interference experiments distinguish between the light sent out on the one hand by a regularly vibrating system of molecules, and on the other hand by irregular short impulses?

6. One of the fundamental facts of our subject is the impossibility of two different sources producing interference phenomena. This fact is generally taken as a proof that molecules must suffer frequent disturbances. But two bodies sending out what we have called regular white light would have the same property. For imagine each of the two sources to send out a series of waves of lengths λ_1, λ_2, &c., differing by quantities which are so small that no instrumental power at our command can resolve them. The illumination at any point of a screen will depend on the manner in which the trains of waves coming from the two sources will combine. The difference of phase between the two sets of waves of length λ_1 depends not only on the relative distance of the sources from the screen, but also on the difference of phase at the two sources. As there is no connexion between that difference of phase for the different wave-lengths, the wave-lengths in close proximity to λ_1 will partly destroy each other, partly have fourfold or any intermediate intensity, the result being the same at all points of the screen as if no interference had taken place. This leads to an important result. Imagine a body, the molecules of which vibrate in a perfectly definite period, but have a translatory motion such as we imagine the molecules of a gas to possess. Such a body would give a spectrum of one line, which, however, would have a certain width owing to the motion of the molecules. The want of homogeneousness produced by this translatory motion would be quite sufficient to prevent the possibility of interference between two similar sources, and we need not take refuge in the impacts between molecules to explain the non-existence of interference.

7. In fig. 1 let L_1 and L_2 be two lenses, H_1 H_2 and K_1 K_2 two screens in their focal plane having small apertures at the foci G and F. If ACB is a grating, a disturbance passing through G will produce a certain effect at F. Unless the relative positions of what for convenience' sake we may call collimator and telescope are adjusted so that a direct image of G is formed at F, the optical lengths of rays such as GBF, GCF, GAF, will not be the same, consequently an instantaneous impulse at G will not remain an instantaneous

Fig. 1.
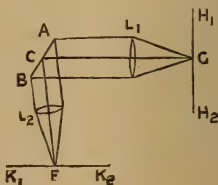
impulse at F, but the light reflected from each line of the grating will reach F at certain intervals of time, and a disturbance will be set up at F which will last during a finite time. The time it takes for an impulse at G to pass completely through F will be that required by light to go over a space equal to the difference in optical length of the extreme rays GBF and GAF. The fact that in every dispersive system an instantaneous impulse entering the system is changed into a disturbance lasting through a finite time is of fundamental importance. It is easily seen that this is brought about in the case of a grating, but the fact is equally true if the dispersion is due to refraction, as will be pointed out further on.

Imagine that in fig. 1 two impulses of the same type succeed each other. If the second impulse begins to reach F before the effects of the first impulse have passed away interference may occur, but if the disturbance due to the first impulse has completely passed through F before the second impulse reaches it, no interference can take place, and this will happen whenever the distance between the impulses before they reach G is greater than the difference in the optical length between the extreme rays GAF and GBF. It is thus seen that if light were to consist of separate instantaneous impulses, interference at the focus of a grating-spectroscope of finite resolving powers could only take place if the retardation were smaller than a certain amount ; if the retardation were greater, no interference could possibly occur.

Now consider the light to be what we have called regular, that is to say, to consist of the superposition of a large number of homogeneous vibrations. If the beam of light is split into two, one being retarded with reference to the other, the spectrum formed in the focal plane of L_2 will be crossed by bright and dark bands ; if the retardation is gradually increased these bands will gradually get nearer and nearer together, and at the same time become less distinct as their distance approaches the limits which are still resolvable by the grating. Looking at it in this general manner, there seems to be no reason why there should be a definite limit when interference ceases, but it would seem as if there ought to be always a fluctuating intensity along the spectrum, although the difference in intensity between the bright and dark bands would with increasing retardation of the interfering beams become so small, that they could no longer be traced. This is the test case previously alluded to, by means of which I originally thought we might distinguish between " regular " and irregular white light. It was found, however, that on actually calculating the difference in intensity between

the maxima and minima of light produced by interference in what we have called regular white light, it is found that, just as in the case of the single impulses, there is a definite limit of retardation, depending on the resolving power of the spectroscope, and if the retardation is increased beyond that limit, the spectrum is perfectly uniform. We shall arrive, therefore, at the conclusion that, both for small and for large resolving powers, any hypothesis we make as to the original production of luminous vibration will lead to the same conclusion. There is no distinction between regular and irregular light beyond that which is brought out by the distribution of intensity in the spectrum. If the intensity vanishes except for a definite wave-length, we must call the vibration completely regular ; if the intensity is the same for all vibrations, it will appear that we must call it completely irregular.

We are prepared now to deduce a formula which will allow us to calculate the disturbance at F (fig. 1), given the disturbance at G.

8. It is convenient to introduce what may be called a " simple grating." An imaginary grating of this kind has

Fig. 2.
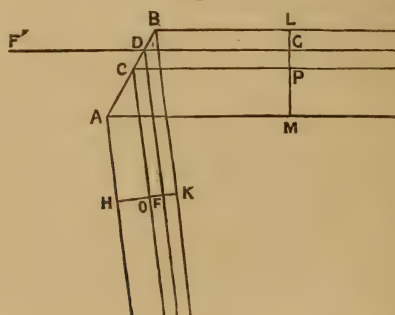
already been made use of by Lord Rayleigh in his article in the *Encyclopædia Britannica**. A simple grating has properties such that a disturbance of unit amplitude is reflected as a disturbance of amplitude $\cos q s$, where q is a constant and s is measured along the grating at right angles to its " lines." In whatever manner the lines of an actual grating are ruled, we may always express the amplitude of the reflected ray as a function of s and obtain that function by means of Fourier's theorem as a sum of terms, one being constant and the others simply periodic ; so that every grating may be treated as a superposition of a number of simple gratings and an ordinary reflecting surface.

* " Wave Theory," § 15.

In fig. 2 let a plane-wave front LM advance towards a grating AB having its centre at C, and let the disturbance at some point of the line PC be given as $f(at)$, t being the time and a the velocity of light. By a proper choice of the origin of time we may express the disturbance at any other point by the same function. If we imagine a telescope pointed in the direction OC, the disturbance at the focus of the object-glass will depend on the disturbance at some previous time over the different points on the line HK at right angles to CO, account being taken only of that part of the disturbance which reaches a point F on HK in a direction DF parallel to CO. Let F′ be a point on CD such that DF′ = DF, and assume that the disturbance at any time which reaches F from D is the same as that which would have reached F′ if the grating had been absent, the amount only being reduced in the ratio $\cos qs$ to unity. The excess of optical length GDF over PCO is $s(\sin \beta - \sin \alpha)$, where α and β are the angles formed by the normal to the grating with CP and CO respectively. Hence if s is measured from C and $f(at)$ is the disturbance at O, the disturbance at F will be

$$\cos qs \, f\{at - s(\sin \beta - \sin \alpha)\}.$$

The amplitude at the focus of the telescope will be proportional to the above expression integrated over the effective aperture. If h be the length of the lines ruled on the grating, $2l$ its width, the integral will become, writing γ for $\sin \beta - \sin \alpha$,

$$h \cos \beta \int_{-l}^{+l} \cos qs \, f(at - \gamma s) \, ds. \quad . \quad . \quad . \quad . \quad (1)$$

It is of course immaterial whether the beam is limited by the grating, or whether we have an infinite grating, and limit the beam by covering the object-glass by a diaphragm of length h and breadth $2l \cos \beta$.

A more rigorous analysis which is given further on (22) will show that the expression which has been deduced when multiplied by a constant factor correctly represents the *amplitude* of the disturbance at the focus of the telescope, if the origin of time is properly chosen, and if $f(at)$ expresses the *velocity* of displacement in the incident beam. The factor by which (1) must be multiplied in order to give correct numerical values is $1/2\pi a F$, where a is the velocity of light and F the focal length of the telescope.

We get a clear idea of the meaning of the integral (1) by its geometrical interpretation. The distance between successive lines of the grating is $2\pi/q$, and if there are 2N lines on the grating it follows that $ql = 2\pi N$; writing $\lambda = 2\pi\gamma/q$ and

changing the variable to $\gamma s = x$, the integral (1) becomes

$$\frac{h \cos \beta}{\gamma} \int_{-N\lambda}^{+N\lambda} \cos 2\pi x/\lambda \, f(at-x) dx. \quad . \quad . \quad (2)$$

For a given position of collimator and telescope, it is known that a homogeneous ray of a certain wave-length will have its principal maximum of the first-order spectrum at the focus of the telescope, and it is easily seen that the wave-length in question is given by the same relation by means of which we have defined λ. Also if $y_1 = f(at)$ is the disturbance at any point of the incident beam, $y = f(at-x)$ will be the disturbance

Fig. 3.
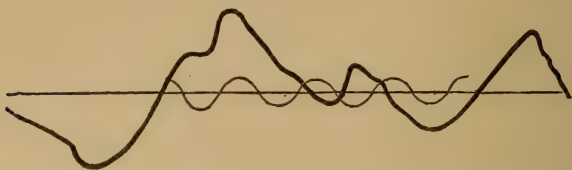
at a distance x, the wave travelling in the positive direction. If, therefore, in fig. 3 the thick line represents the shape of a wave travelling from left to right, and the thin line is the cosine curve $y_2 = \cos 2\pi x/\lambda$, having as many periods as there are lines on the grating, the disturbance at the focus of the telescope is proportional to $\int y_1 y_2 \, dx$.

The disturbance at all times is obtained by letting the wave travel forward, the cosine curve remaining in the same position.

9. We shall use equation (1) as the basis of our calculations. It is required to find the disturbance at F (fig. 1) for any given position of the telescope. We may define the position either by the quantity λ or by $q = 2\pi\gamma/\lambda$; when convenient we shall introduce the number of lines on the grating $2N = ql/\pi$.

As a first example, let $f(at) = p \cos pt$, that is to say, let the incident beam be homogeneous, the maximum displacement being unity. Leaving out constant factors, the integral to be determined is

$$\int_{-l}^{+l} p \cos qs \cos(pt - \kappa s) ds,$$

where κ is written shortly for $p\gamma/a$.

Remembering that ql is a multiple of 2π, the integral is easily seen to become

$$\frac{2qp}{q^2 - \kappa^2} \sin \kappa l \cos pt. \quad . \quad . \quad . \quad . \quad (3)$$

It follows that, whatever the direction of the telescope, the disturbance passing through its focus is of the same period as that of the incident light, that is to say, whatever the periodicity of the grating it has no power of altering the periodicity of the disturbance. The amplitude of the disturbance is $\frac{2pq}{q^2-\kappa^2}\sin\kappa l$. The manner in which this varies according to the direction of the telescope is shown by expressing l in terms of N, when it is seen that we may write for the amplitude

$$\frac{2pql}{\kappa\pm q}\ \frac{\sin[2\pi N(\kappa\mp q)/q]}{2\pi N(\kappa\mp q)/q}.$$

The second factor is of the form $(\sin\alpha)/\alpha$, which reaches its maximum value when $\alpha=0$. The successive maxima are very close together if N is large, so that the whole light is near the points for which $\kappa=\pm q$. The direction of the optic axis in that case is given by $\pm qa=p\gamma$. The wave-length of the original light being $\mu=2\pi a/p$ and the distance between the lines $d=2\pi/q=2\pi/\kappa$, the relation becomes

$$\mu=d\gamma=\pm d(\sin\alpha-\sin\beta),$$

which is the well-known condition that a wave-length μ shall have a first-order maximum in the direction defined by β. The other maxima of $(\sin\alpha)/\alpha$ which our equation gives are those commonly ascribed to diffraction from the edge of the aperture of the telescope.

The principal maximum has an amplitude which, restoring the constant factors, is $plh\cos\beta/2\pi aF$, or, introducing the wave-length μ of the incident light, the amplitude becomes $hl\cos\beta/F\mu$. The numerator of this fraction is half the effective aperture of the grating, and the intensity of the spectrum is therefore one quarter of what it would be if the grating were replaced by a reflecting surface, and the collimator moved until the direct image coincided with the focus of the telescope. A surface which acts like a grating must also, as pointed out by Rayleigh, act as an absorbing surface, so that the sum of the intensities in the diffracted spectra will be smaller than that of the original light.

10. Ordinary gratings are generally taken to contain parts which are alternately completely reflecting or transparent and opaque. Calling d the distance from the centre of one line to the centre of the next, and taking the origin at the centre of one of the lines, we may express the reflecting properties of the grating (confining ourselves to reflecting gratings) as a periodic function of x, say $f(x)$, which may be expressed in a series of the form

$$\frac{b_0}{2} + b_1 \cos \frac{\pi x}{d} + b_2 \cos \frac{2\pi x}{d} + \ldots$$

where

$$b_m = \frac{2}{d} \int_0^d f(\lambda) \cos \frac{m\pi\lambda}{d} d\lambda.$$

Let the reflecting part cover a portion $2a$ of the grating, and the opaque part a portion $2c$. The function to be expanded has a value one from $x=0$ to $x=a$; the value will vanish between $x=a$ and $x=a+2c$, and regain the unit value from $x=d-a$ to $x=d$.

We find in this way,

$$b_m = \frac{2}{m\pi} (1 + \cos m\pi) \sin \frac{m\pi a}{d},$$

or if, as in the previous investigation, we put $d=2\pi/q$,

$$f(x) = \frac{qa}{\pi} + \frac{2}{\pi} \left[\sin aq \cos qx + \frac{1}{2} \sin 2aq \cos 2qx + \frac{1}{4} \sin 4aq \cos 4qx + \ldots \right.$$

The first term represents that part of the grating which acts simply as a reflecting surface. In order that the first-order spectrum should be as bright as possible $\sin aq = 1$, or $d = 4a$, in which case the spectra of even orders would all disappear. The factor $2/\pi$, taken in conjunction with what we have previously proved, shows that a grating constructed in the manner indicated gives a first-order spectrum whose intensity cannot exceed A/π^2, where A is the intensity of the reflected image, if there are no lines on the grating. The strongest second-order spectrum has an intensity $A/4\pi^2$.

The direct image could be much diminished, and therefore the spectra increased in intensity, if a grating could be made on a glass surface—say the largest surface of a right-angled prism,—periodicity being introduced by silvering the glass along parallel lines. If light were then allowed to fall internally on the silvered surface, the reflexions taking place between glass air and glass silver respectively would have nearly opposite phases, which is the condition required for the diminution of intensity of the direct image.

It appears, then, that although we have introduced an imaginary grating called a simple grating, the effects are exactly the same as those of a real grating, the latter consisting of a superposition of simple gratings, as has already been pointed out.

11. We return now to our more immediate object, and take as a second example of a disturbance analysed by a grating that of a single impulsive velocity v reaching the point O

(fig. 2) at a time t_1, and lasting during an interval of time τ, the displacement produced by the velocity being $c = v\tau$.

The value of $f(at - \gamma s)$ will vanish in this case unless $at - \gamma s = at_1$, which condition determines some point along s at which the disturbance is sensible, provided that t lies between $t_1 - \gamma l/a$ and $t_1 + \gamma l/a$. The integral (1) therefore becomes

$$\frac{hac \cos \beta}{\gamma} \cos \left[qa(t - t_1)/\gamma \right] = \frac{hac \cos \beta}{\gamma} \cos \left[2\pi N a(t - t_1)/\gamma b \right].$$

The equation applies while t lies between the stated limits ; for smaller or greater values of t the disturbance vanishes. Taking account of the omitted factor, the disturbance is seen to begin with an impulsive displacement, $\dfrac{hc \cos \beta}{2\pi a \gamma F}$, followed by a simple vibration continuing for as many periods as there are lines on the grating, ending with a permanent displacement c. While the disturbance lasts it is of the same nature as a homogeneous vibration having a wave-length $\gamma l/N$, and as N/l is the distance between the lines of a grating we may express our result as follows :—

The disturbance produced by a single impulse leaving the focus of the collimator when resolved by a grating and telescope will, at the focus of the telescope, consist of a succession of oscillations equal in number to the lines of the grating and having the same period as that homogeneous vibration which, leaving the collimator, would have its principal maximum at the focus of the telescope.

It would be wrong to speak of such vibrations as homogeneous, although for a certain time they may be analytically represented by a sine function. This has repeatedly been pointed out by Lord Rayleigh, and a good deal of the difficulty which has been felt on the subject is due to our natural inclination to consider as homogeneous a train of waves which for a finite space coincides with the curve $y = \cos \kappa x$. Such a train is the more homogeneous the greater the space for which the equation holds, and our grating will give at the focus of the telescope light which is the more homogeneous the greater the number of lines.

12. It will be instructive to take as a third example the case of such a finite succession of waves as we have just spoken of, and see what the grating will make of it.

We put $f(at) = 0$ for all values of t smaller than t_1 and greater than t_2, while between these values of t the velocity $f(at)$ shall be equal to $p \cos pt$. If at the time t_1 there is no discontinuity of displacement, we must put $\cos pt_1 = 1$; and if the train consists of m complete waves, $p(t_2 - t_1) = 2\pi m$.

We have to find the value of

$$\int p \cos qs \cos (pt - \kappa s)ds,$$

and must for that purpose divide the integral into three parts. During the first period the train of waves will have encroached on the grating, and the limits of the integral during that period will be $-l$ and that value of s, viz. $a(t-t_1)/\gamma$, at which $f(at-\gamma s)$ ceases to vanish. During the second period the complete train of waves will intersect the grating, and the limits of the integral will be $a(t-t_2)/\gamma$ and $a(t-t_1)/\gamma$. During the third period the disturbance will pass off the grating.

It is not necessary to give the details of the calculation. During the first period the disturbance is expressed by

$$\frac{p\kappa}{q^2-\kappa^2} \sin qa(t-t_1)/\gamma - \frac{qp}{q^2-\kappa^2} \sin (pt + \kappa l) ;$$

that is, the disturbance may be expressed as a superposition of two trains of waves, one having a period equal to that of the incident light and the other determined by the direction of the diffracted beam. If the telescope is pointed towards the principal maximum of light, the expression reduces to

$$\frac{p}{2}\left[a(t-t_1)/\gamma + l\right] \cos pt,$$

and represents a vibration with variable amplitude. The factor in square brackets vanishes when the disturbance first reaches the grating, and after m complete vibrations becomes

$$(m\pi p/\kappa) \cos pt.$$

From that time onwards we have to change the limits of integration, and the amplitude of the disturbance is then expressed by

$$\int_{a(t-t_2)/\gamma}^{a(t-t_1)/\gamma} p \cos qs \cos (pt - \kappa s)ds$$
$$= p \sin \pi mq/\kappa \left[\frac{\cos (qat/\gamma - \phi)}{q-\kappa} + \frac{\cos (qat/\gamma - \psi)}{q+\kappa}\right].$$

In this equation ϕ stands for $\dfrac{(q-\kappa)at_1}{\gamma} + \dfrac{\pi mq}{p}$, and ψ for $\dfrac{(q+\kappa)at_1}{\gamma} + \dfrac{\pi mq}{p}$. The difference in phase between the two vibrations is therefore $2\kappa at_1/\gamma = 2pt_1$. But as $\cos pt_1 = 1$, this only means that the two vibrations have the same phase.

Hence the amplitude will be

$$\frac{2pq}{q^2-\kappa^2} \sin \pi mq/\kappa.$$

The maxima of light take place when $q = \kappa$, and the amplitude of the principal maximum is $2mp/(q + \kappa)$. If this is compared with the amplitude of the principal maximum formed when an infinite train of waves falls on a finite grating, it is easily seen that : The position of the principal maximum and the amplitude at the principal maximum are the same whether an infinite train of waves falls on a grating containing 2N lines or whether the grating is considered infinite and the train of waves is limited to 2N complete waves. If we compare the time of vibration instead of the amplitude, we must note an important difference in the two cases. With an unlimited train of waves falling on a finite grating the period is everywhere the same as in the incident light ; but when the train of waves is limited, the period is that determined by the position of the telescope. At the principal maximum the two periods agree ; at other places they differ.

13. We may now consider the case of two disturbances of the same type following each other after an interval 2τ. If both consist of a single impulsive velocity, our previous result can at once be applied. Such an impulse will at the focus of a telescope produce as many oscillations as there are lines on the grating, the complete time τ' of each oscillation depending on the position of the focussing lens. The disturbance will therefore last through a time $2N\tau'$, and as long as $\tau < N\tau'$ interference will take place—that is, the two trains of waves will partially cover each other, and according to the relative value of τ' and τ the energy during the period of overlapping may be greater or smaller than the energy of the original vibrations. But as soon as $\tau \geqq N\tau'$, the waves are clear of each other and no interference can take place.

Let us now treat the same problem, taking the white light to be " regular," that is, to give an ultimately discontinuous spectrum of homogeneous vibrations.

We take the maximum velocity of the incident light to be the same for all wave-lengths, in order to make it more closely correspond to the single impulsive velocity, which, when resolved by Fourier's theorem, draws no distinction between different wave-lengths. The original disturbance, consisting of two trains of waves following each other at a time 2τ, is now expressed by

$$f(at) = \cos pt + \cos p(t - 2\tau),$$

from which the disturbance at the focus of the telescope is obtained as in (3) and found to be

$$\frac{2q}{q^2 - \kappa^2} \sin \kappa l [\cos pt + \cos p(t - 2\tau)].$$

This represents an oscillation having a maximum velocity

$$\frac{4qp}{q^2 - \kappa^2} \sin \kappa l \cos p\tau.$$

If the energy contained within a region $d\lambda$ of the original light is $B d\lambda$, where B is a constant, the energy contained within the region defined by p and $p + dp$ will be $2\pi B a \, dp/p^2$.

The square of the maximum velocity may be taken as a measure of the energy transmitted in a given time. Changing the variable to κ by the relation $p = a\kappa/\gamma$, and introducing $r = a\tau/\gamma$, the total energy E of the separate trains of waves passing through a small area s at the focus of the telescope may, when their number becomes large, be expressed as an integral. To get correct results we must restore the omitted factor $\dfrac{h \cos \beta}{2\pi a F}$ in the amplitude of the disturbance, and writing $A = B h^2 \cos^2 \beta / F^2 \gamma$,

$$E = \frac{8}{\pi} A s \int_0^\infty \frac{q^2 d\kappa}{(q^2 - \kappa^2)^2} \sin^2 \kappa l \cos^2 \kappa r.$$

In order to find the value of this integral, we transform it as follows :—

$$\int_0^\infty \frac{q^2 d\kappa}{(q^2 - \kappa^2)^2} \sin^2 \kappa l \cos^2 \kappa r$$

$$= \int_0^\infty \frac{d\kappa}{(q^2 - \kappa^2)} \sin^2 \kappa l \cos^2 \kappa r + \int_0^\infty \frac{\kappa^2 d\kappa}{(q^2 - \kappa^2)^2} \sin^2 \kappa l \cos^2 \kappa r$$

$$= \int_0^\infty \frac{d\kappa}{(q^2 - \kappa^2)} \sin^2 \kappa l \cos^2 \kappa r - \frac{1}{2} \int_0^\infty \frac{d\kappa}{(q^2 - \kappa^2)} \frac{d}{d\kappa} (\kappa \sin^2 \kappa l \cos^2 \kappa r)$$

$$= \frac{1}{2} \int_0^\infty \frac{d\kappa}{(q^2 - \kappa^2)} \sin^2 \kappa l \cos^2 \kappa r - \frac{1}{2} \int_0^\infty \frac{\kappa d\kappa}{(q^2 - \kappa^2)} (l \sin 2\kappa l \cos^2 \kappa r$$
$$- r \sin 2\kappa r \sin^2 \kappa l).$$

The values of these definite integrals are easily found by expanding in Fourier series functions which between 0 and l shall be expressed by $\sin 2qx$ or $\cos 2qx$, and vanish for $x > l$. The general equations which are applicable here are :

$$\phi(x) = \frac{4}{\pi} \int_0^\infty \int_0^l \phi(\lambda) \cos 2\kappa x \cos 2\kappa l \, d\kappa \, d\lambda$$

$$= \frac{4}{\pi} \int_0^\infty \int_0^l \phi(\lambda) \sin 2\kappa x \sin 2\kappa l \, d\kappa \, d\lambda.$$

Putting $\phi(x) = \sin 2qx$ or $\cos 2qx$, with the condition that $\cos ql = 1$, we obtain the following four equations, which will hold for all values between $x = 0$ and $x = l$, but not necessarily at the limits.

$$\sin 2qx = \frac{4}{\pi}\int_0^\infty \frac{q\,d\kappa}{q^2-\kappa^2}\sin^2\kappa l \cos 2\kappa x,$$

$$= \frac{2}{\pi}\int_0^\infty \frac{q\,d\kappa}{\kappa^2-q^2}\sin 2\kappa l \sin 2\kappa x,$$

$$\cos 2qx = \frac{2}{\pi}\int_0^\infty \frac{\kappa\,d\kappa}{\kappa^2-q^2}\sin 2\kappa l \cos 2\kappa x,$$

$$= \frac{4}{\pi}\int_0^\infty \frac{\kappa\,d\kappa}{\kappa^2-q^2}\sin^2\kappa l \sin 2\kappa x.$$

If $0 < x < l$ and $\sin ql = 0$.

The first two integrals will hold for $x=0$, as the left-hand side vanishes at that point; the right-hand side will therefore vanish for indefinitely small positive values, and consequently also for indefinitely small negative values. The third equation will also hold for $x=0$, as both sides give the same value for positive and negative values of x. The fourth equation, however, does not hold at the same point. Putting $x=0$ in the first and third integrals, we obtain

$$0 = \int_0^\infty \frac{q\,d\kappa}{q^2-\kappa^2}\sin^2\kappa l,$$

$$1 = \frac{2}{\pi}\int_0^\infty \frac{\kappa\,d\kappa}{\kappa^2-q^2}\sin 2\kappa l.$$

Combining these with the previous results, we easily deduce the following:—

$$1 + \cos 2qx = \frac{4}{\pi}\int_0^\infty \frac{\kappa\,dk}{\kappa^2-q^2}\sin 2\kappa l \cos^2\kappa x,$$

$$1 - \cos 2qx = \frac{4}{\pi}\int_0^\infty \frac{\kappa\,d\kappa}{\kappa^2-q^2}\sin 2\kappa l \sin^2\kappa x,$$

$$\sin 2qx = \frac{8}{\pi}\int_0^\infty \frac{q\,d\kappa}{q^2-\kappa^2}\sin^2\kappa l \cos^2\kappa x.$$

If $0 < x < l$, and $\sin ql = 0$.

$$\frac{\pi}{4} = \int_0^\infty \frac{\kappa\,d\kappa}{\kappa^2-q^2}\sin 2\kappa l \cos^2\kappa x,$$

$$\frac{\pi}{4} = \int_0^\infty \frac{\kappa\,d\kappa}{\kappa^2-q^2}\sin 2\kappa l \sin^2\kappa x,$$

$$0 = \int_0^\infty \frac{q\,d\kappa}{q^2-\kappa^2}\sin^2\kappa l \cos^2\kappa x.$$

If $x > l$ and $\sin ql = 0$.

But if the value of r exceeds that of l, the integrals have different values.

With the help of these equations we find, if $r < l$,

$$E = \frac{As}{2q} \left[\sin 2qr + 2ql + 2q(l-r) \cos 2qr \right].$$

The first term may be neglected compared to the two others if the number of lines on the grating is great, and we may without appreciable error write

$$E = As[l + (l-r) \cos 2qr].$$

This equation, however, only holds when l exceeds r. If, on the other hand, $r > l$, the definite integrals on which E depends take different values, which give in that case

$$E_0 = Asl.$$

The expression for the energy here does not involve r, and therefore whatever the retardation the energy is the same, and the spectrum will show neither minima nor maxima. The point at which interference ceases is given by $r = l$, that is by $\tau = \gamma l/a$; γl being the difference in optical length between the extreme rays which fall on the grating, the value of τ is identical with that for which interference ceases in the case of a simple luminous impulse. Thus Gouy and Rayleigh's proposition is proved for the case of a finite grating. Interference ceases completely for a given retardation of path depending only on the resolving power of the grating and not on the nature of the light. Our test case is therefore disposed of, but it is not easy to see how we could have foreseen the result without the complete analysis.

14. The expression for the energy may with advantage be transformed by taking as the area s that included within a slit parallel to the lines of the grating, the edges of the slit coinciding with the principal maxima of the two wavelengths λ and $\lambda + d\lambda$. The illumination along the slit will show maxima and minima distributed in a well-known manner, the beam being limited by a rectangular aperture. If x is measured along the slit and the intensity is taken as unity at the central point, the intensity at any other point will be

$$\frac{\sin^2 \dfrac{\pi h x}{\lambda F}}{\dfrac{\pi^2 h^2 x^2}{\lambda^2 F^2}},$$

h being the height of the slit. If this is integrated between infinite positive and negative values of x, the result is found to be $\lambda F/h$. This is the quantity by which we must multiply our expression if the whole energy passing through the slit is required. As regards the width of the slit we connect in the first place λ and β by the relation

$$\lambda = \frac{2\pi}{q} (\sin \beta - \sin \alpha),$$

and hence

$$d\lambda = \frac{2\pi}{q} \cos \beta \, d\beta.$$

F being the focal length of the telescope, the interval separating the principal maxima of the two wave-lengths λ and $d\lambda$ of the slit will be

$$F d\beta = F q \, d\lambda / (2\pi \cos \beta).$$

Hence

$$E_0 = A F q^2 l \lambda d\lambda / (2\pi h \cos \beta)$$
$$= B q h l \lambda \cos \beta \, d\lambda / (2\pi \gamma),$$

and as $\lambda q = 2\pi\gamma$,

$$E_0 = B h l \cos \beta \, d\lambda = \tfrac{1}{2} B s \, d\lambda,$$

where s is the effective surface of the telescope, and $B d\lambda$ the energy per unit surface within the limits specified by $d\lambda$. As was shown previously for a single homogeneous vibration, the energy contained in the first-order spectrum is one quarter of that which would reach the focus of the telescope if the grating were replaced by an ordinary reflecting surface.

It must of course be remembered that in the last case we have been dealing with a succession of two sets of waves for each of which the energy per unit surface has been put equal to $B d\lambda$.

Returning to the smaller retardation for which the spectrum is crossed by dark and bright bands, we may conveniently write the energy passing through the slit between the wavelengths λ and $\lambda + d\lambda$

$$E = \tfrac{1}{4} \frac{B s \, d\lambda}{N\lambda} \left[D + 2\left(\frac{2N\lambda}{\lambda} - D\right) \frac{\cos^2 \pi D}{\lambda} \right],$$

where D stands for the retardation expressed as a length.

From this we obtain

$$\frac{E_{(minimum)}}{E_{(maximum)}} = \frac{D}{4N\lambda - D},$$

which holds as long as the retardation is smaller than the product of the wave-length into the number of lines (2N) on the grating. If $D = 2N\lambda$ the equation shows that there is no difference between the minimum and maximum, and this continues for greater values of D. The importance of the equation lies in the fact that it is applicable whatever the nature of the light, as long as the intensity does not change rapidly along the spectrum. We may write the expressions in a form in which they are applicable to the spectra of different orders and also to spectra formed by prisms. If we take as the limit of revolution of two lines of wave-lengths λ and $\lambda + d\lambda$ that in which the principal maximum of one falls on the first minimum of the other, Rayleigh has shown * that in the first-order spectrum two lines are resolved when

$$\frac{d\lambda}{\lambda} = \frac{1}{2N}.$$

If we take $\lambda/d\lambda$ as the measure of the resolving power (R) of the spectroscope we may write R for 2N. If we further express the retardation N in terms of wave-length, so that $D = n\lambda$ where n may be a fraction, the distribution of intensity in the spectrum may be written

$$E = C\left[\frac{n}{R} + 2\left(1 - \frac{n}{R}\right)\cos^2 n\pi\right]d\lambda = C\left[1 + \left(1 - \frac{n}{R}\right)\cos 2n\pi\right]d\lambda,$$

where C is a constant and the relation between the maxima and minima becomes

$$\frac{E_{min.}}{E_{max.}} = \frac{n}{2R - n}. \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (4)$$

15. I have treated, so far, only of grating spectra. The investigation in detail of the effects produced by prisms is more complicated, but it is easy to see that there can be no essential difference between the two cases. If we possessed a substance which, when cut into the form of a prism, would separate the wave-lengths laterally according to the same law as the grating, the disturbance at the focus of the telescope attached to a prism spectroscope would be exactly the same as if the prism were replaced by a grating of the same resolving power. But whatever the law of dispersion the condition is approximately fulfilled within that small region of wave-lengths which adds appreciably to the disturbance at any point. A separate treatment of prisms would therefore seem unnecessary.

* *Encyclopædia Britannica*, " Spectroscopy."

But there is a point of view sufficiently instructive in my opinion to be mentioned. In the case of a grating it is easy to see how a solitary impulse is spread out into a disturbance lasting a finite time—it is not so clear that the same holds for a prism. The easiest way to assure ourselves that a prism acts in the same way as a grating, is to cease to consider only homogeneous waves and to follow through the prism a group of waves involving, as it always does, oscillations of different periods.

Let us imagine a train of waves made up of a finite number of oscillations, each following the law of a simple pendulum. The analytical representation of such a group will introduce wave-lengths which do not differ much. The front or rear of such a train of waves may be taken to pass through a medium like glass with a definite velocity, which is the group velocity corresponding to the given range of wave-lengths. In fig. 4 let A B be the direction of the front of the incident wave, C D that of the emergent wave, then, as the group velocity in the prism is smaller than the wave velocity, the front of the group will after emergence be parallel to some such direction as D K. If the light is concentrated by means of a lens, the position of the focus is determined by the condition of agreement of phase; that is to say, the optical length from all points C D to the focus must be the same, but in that case the optical length from the different points of K D will not be the same,—in other words, the front of the wave will take some time to pass through the focus, just as it would if the spectrum were produced by a grating. The same holds for the rear of the group and for any disturbance, account being taken of the different group velocities for different regions of the spectrum. To make the analogy with the grating more complete, let us calculate the distance C K through which the group has fallen behind the front. The group velocity U is connected with the wave-velocity V by

Fig. 4.

$$U = \frac{d\kappa V}{d\kappa},$$

where κ is inversely proportional to the wave-length. The difference in the two velocities is therefore

$$V - U = \frac{\lambda d V}{d\lambda}.$$

The wave-front will pass through a thickness t of the prism

in time t/V, the group-front in a time t/U. The difference in time is $t(V-U)/UV$, which, as V and U do not differ much, we write approximately $t(V-U)/V^2$. If t represents the effective thickness of the prism, the distance CK, through which the group is displaced, will be, remembering that μV is the velocity in air,

$$CK = \frac{\mu t(V-U)}{V} = \frac{\mu t\lambda}{V}\frac{dV}{d\lambda} = \frac{\mu t\lambda}{V}\frac{dV}{d\mu}\frac{d\mu}{d\lambda}$$

$$= -t\lambda \frac{d\mu}{d\lambda}.$$

It has been shown by Rayleigh that the resolving power (R) of a prism defined as in (14) is $t\dfrac{d\mu}{d\lambda}$, so that the displacement CK of the group will be

$$CK = R\lambda,$$

just as in the case of a grating.

What holds for the group front and rear will also hold for any portion of the group in so far as it is made up of wavelengths differing only to a small extent from the one under consideration. The analogy between a prism and a grating of the same resolving power is therefore complete.

16. The consideration of the group-front instead of the wave-front in optical systems leads to known results in a somewhat novel and instructive way. Thus a lens (fig. 5) will convert a plane front HK into a spherical front ACB; but the group-front will be distorted into a form such as AC'B ; where CC' depends on the thickness of the lens. The

Fig. 5.
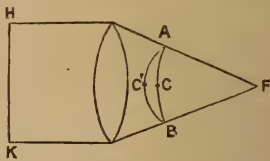
displacement does not alter the focus but it interferes with the definition of the image. The want of definition thus produced is known as chromatic aberration. Chromatic aberration may partially be corrected by joining two lenses of different materials. From our point of view a lens is achromatic when the time taken from the original wave-front to the focus F is the same along all paths for the *group*-fronts as well as for the *wave*-fronts ; and it is easily shown that this condition will lead to the well-known relation for achromatism. It must be understood of course that the group-front differs from the wave-front in the important particular that the phases at different points of the group-front are not the same. In a

group of waves the waves move through the group, and the configuration of the group changes. We can speak of definite rate of propagation (U) of the group, because at definite intervals τ the group takes up the same shape displaced through a distance Uτ. A good idea of some of the phenomena of group velocities may be obtained by considering a medium in which the wave-velocity varies as a linear function of the wave-length, for in that case the group velocity is independent of the period; but the discussion of this subject must be reserved for a separate communication.

17. It will be useful at this stage to inquire in what cases we can legitimately apply the word "interference" to an optical phenomenon. The essence of interference is the independence of superposed vibrations; in other words, the most important point of an interference phenomenon is that there is *no* interference as regards amplitude. There may, however, be interference as regards energy.

If a wave-front is propagated, we may say that this implies interference, for if the different points of the wave-front acted as separately vibrating points, and we summed up for energy instead of for amplitude, a very different result from that actually obtained would be arrived at. Diffraction may in this way be said to be the absence of interference. But in speaking of interference phenomena we may reasonably leave out of account that which is involved in the propagation of a wave-front.

Consider a succession of separate but exactly similar impulses, such as is shown in fig. 6. If the different disturbances do not overlap, there can be no interference between them. But if each impulse is analysed by Fourier's theorem, the

Fig. 6.

different wave-lengths will be represented with different intensities. If the *sum* of the disturbances is analysed, the relative intensity of the different terms of the series will be modified, and considerably so if the impulses are numerous and succeed each other at regular intervals. The leading term in the expansion will be that having a wave-length equal to the distance between the impulses. From the point of view of Fourier's series, we may say that the different disturbances have "interfered," but the series being only a mathematical representation of the curve shown in the figure, I think the term interference would be misleading. We shall reserve the word interference exclusively for the case that the total energy

contained in the disturbance is not equal to the sum of the energies contained in its different parts.

If such a succession of waves as we have been speaking of were to fall on the retina of our eye, a colour-effect might be produced by the combination where none is produced by the individual disturbance. In that case there is interference; but it will be shown that the interference is due to some resonance effect in the eye, but does not exist objectively.

18. We proceed to discuss the nature of interference produced when some point of a screen is illuminated by two different sources of light. Let the velocity due to each source separately be expressed as functions of the time, $f(t)$ and $\phi(t)$, the velocity at any time due to the superposition of the two disturbances is $f(t) + \phi(t)$, and the excess of kinetic energy of the combination over the sum of the energies due to each separately will be proportional to

$$[f(t) + \phi(t)]^2 - [f(t)^2 + \phi(t)^2] = 2f(t)\phi(t).$$

The value of

$$2 \int_{-\infty}^{+\infty} f(t)\phi(t)\,dt$$

may be taken as a measure of the "interference." In order to express this in a form suitable for our purpose, we make use of the well-known proposition expressed by the equation

$$\text{Limit } (h = \infty) \quad \int_{\alpha}^{\beta} f(x) \frac{\sin h x}{x}\,dx = \begin{cases} \frac{\pi}{2} f(0), \text{ if } \beta \text{ positive and } \alpha = 0 \\ 0 \text{ if } \beta > \alpha > 0. \end{cases}$$

From this we easily obtain, if u is a positive quantity,

$$\text{Limit } (h = \infty) \quad \int_{0}^{\infty} f(x) \frac{\sin h (x-u)}{(x-u)}\,dx = \pi f(u).$$

Let $\mathrm{F}(\lambda_1, \lambda_2)$ be a function of two independent variables, and consider the integral

$$\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{0}^{\infty} \mathrm{F}(\lambda_1, \lambda_2)\cos \kappa(\lambda_1 - \lambda_2)\,d\lambda_1\,d\lambda_2\,d\kappa.$$

Performing the integration with respect to κ, we find

$$\text{Limit } (\kappa = \infty) \quad \int_{-\infty}^{\infty}\int_{-\infty}^{\infty} \mathrm{F}(\lambda_1, \lambda_2) \frac{\sin \kappa (\lambda_1 - \lambda_2)}{(\lambda_1 - \lambda_2)}\,d\lambda_1\,d\lambda_2;$$

and this, with the help of the above relation, becomes

$$\pi \int_{-\infty}^{\infty} \mathrm{F}(\lambda_1, \lambda_1)\,d\lambda_1,$$

where $F(\lambda_1, \lambda_1)$ means the function into which F is changed by substituting everywhere λ_1 for λ_2. If, therefore, we transform a function of one variable t, $F(t)$, into one of two variables t and t', $F(t,t')$, by simply writing t' for t in part of the expression, we may put

$$\pi \int_{-\infty}^{+\infty} F(t) dt = \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \int_{0}^{+\infty} F(\lambda_1, \lambda_2) \cos \kappa(\lambda_1 - \lambda_2) \, d\lambda_1 \, d\lambda_2 \, d\kappa.$$

If we apply this to the product $f(t)\phi(t)$ we find

$$\pi \int_{-\infty}^{+\infty} f(t) \phi(t) dt = \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \int_{0}^{\infty} f(\lambda_1) \phi(\lambda_2) \cos \kappa (\lambda_1 - \lambda_2) d\lambda_1 d\lambda_2 d\kappa.$$

The theorem expressed by this equation may be written

$$\pi \int_{-\infty}^{+\infty} f(t) \phi(t) dt = \int_{0}^{+\infty} (A_1 A_2 + B_1 B_2) d\kappa \; ;$$

where

$$A_1 = \int_{-\infty}^{+\infty} f(\lambda) \cos \kappa \lambda \, d\lambda, \qquad B_1 = \int_{-\infty}^{+\infty} f(\lambda) \sin \kappa \lambda \, d\lambda,$$

$$A_2 = \int_{-\infty}^{+\infty} \phi(\lambda) \cos \kappa \lambda \, d\lambda, \qquad B_2 = \int_{-\infty}^{+\infty} \phi(\lambda) \sin \kappa \lambda \, d\lambda.$$

The special case in which the two functions f and ϕ are equal has been proved by Rayleigh (Phil. Mag. xxvii. 1889). The excess of energy of two trains of waves over that of the separate ones is thus seen to depend in a simple way on the analysis of each by Fourier's theorem. If the two trains are of the same type, one following the other at an interval of time 2τ, we can put the excess of energy E into the form

$$\frac{\pi}{2} E = \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \int_{0}^{\infty} f(\lambda_1 + \tau) f(\lambda_2 - \tau) \cos \kappa(\lambda_1 - \lambda_2) \, d\lambda_1 \, d\lambda_2 \, d\kappa.$$

Substituting $\mu_1 = \lambda_1 + \tau$, $\mu_2 = \lambda_2 - \tau$, this becomes

$$\frac{\pi}{2} E = \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \int_{0}^{\infty} f(\mu_1) f(\mu_2) \cos \kappa (\mu_1 - \mu_2 - 2\tau) \, d\mu_1 \, d\mu_2 \, d\kappa$$

$$= \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \int_{0}^{\infty} f(\mu_1) f(\mu_2) \cos 2\kappa\tau \cos \kappa (\mu_1 - \mu_2) \, d\mu_1 \, d\mu_2 \, d\kappa,$$

or if $A = \int_{-\infty}^{+\infty} f(\mu) \cos \kappa \; d\mu$, $B = \int_{-\infty}^{+\infty} f(\mu) \sin \kappa \mu \, d\mu$,

$$\frac{\pi}{2} E = \int_{0}^{\infty} (A^2 + B^2) \cos 2\kappa\tau \, d\kappa. \quad . \quad . \quad . \quad . \quad (5)$$

But $(A^2 + B^2) d\kappa$ is proportional to that part of the energy

which lies within the range $d\kappa$, and the amount of interference is therefore seen to depend on the distribution of energy only and not on any assumption respecting the regularity or irregularity of vibration.

19. We may apply our result to some special case. The simplest experimental arrangement to obtain a double source is that of placing a point from which light diverges close to a mirror as in Lloyd's experiment, and we may imagine the radiation to be received on a screen at right angles to the mirror and the energy to be measured by means of a thermopile or bolometer. As the distribution of energy will entirely depend on the law connecting radiation and wave-length, we must introduce some assumption concerning the connexion. The simplest law is that ascribed by Rayleigh to H. F. Weber, according to which the energy contained within a region $d\kappa$ of the spectrum is

$$Ce^{-a^2\kappa^2}d\kappa,$$

where C and a are constants and $2\pi/\kappa$ means the time of vibration.

The excess of energy E of the double source over the separate sources is from (5)

$$\frac{\pi}{2}E = \int_0^\infty Ce^{-a^2\kappa^2}\cos 2\kappa\tau \, d\kappa,$$

$$E = \frac{C}{a\sqrt{\pi}}e^{-\tau^2/a^2}.$$

If the source of light is a slit parallel to the mirror and x the distance of any point on the screen from the mirror, the excess of energy contained in a strip of width dx would be Edx, and τ, which is half the retardation in time of the light reaching the screen from the two sources, is proportional to x. Hence changing the value of C and a, we may say that the excess of energy of the double source over the effects of the single sources acting independently is

$$\frac{C}{a\sqrt{\pi}}e^{-x^2/a^2}dx.$$

The energy is seen to be greatest at the screen and to fall off quickly towards the side. The excess of energy is everywhere positive, or the total energy is increased by the presence of the mirror. There is nothing intrinsically impossible in this result. A source of sound will do more work when placed close to a wall than if the wall were absent. If effects of the same nature are generally not observed in the case of light, it is due to the smallness of the wave-length of the radiation

which constitutes light. But any law connecting radiation and wave-length must take in all ranges of waves, and the particular law adopted gives finite values of intensity within a finite range of κ even for infinitely long waves, hence the result we have obtained was only to have been expected. It may be said, of course, that we have assumed our wall to be a perfect reflector for all wave-lengths; but it is not necessary to enter into this question any further, as, for other reasons, Weber's law cannot be reconciled with experiment. H. F. Weber himself really uses his law in two contradictory senses and seems to have overlooked the great difference there is in the distribution of energy in a spectrum according as a prism or a grating is used to analyse the light. Weber takes as his measure of energy the energy contained in the "homogeneous radiation of wave-length λ." If the quantity given by Weber is denoted by S, Rayleigh interprets his meaning to be that the energy within a range $d\lambda$ is $S d\lambda$, and in the discussion of Langley's observations Weber uses his law in that sense; but Weber also draws conclusions favourable to his equation from the fact that Tyndall, using a prism, observed the maximum heating-effect of an arc-spectrum at a particular place and uses his formula as if the energy contained within a range $d\mu$ (μ being the refractive index) was $S d\mu$.

If the more natural interpretation of Weber's formula is the right one, there should be no maximum of energy in a spectrum formed by a prism at all, but the intensity should indefinitely increase with the wave-length. For μ and κ being approximately connected by the relation

$$\mu = \mu_0 + c\kappa^2, \qquad d\mu = 2c\kappa d\kappa,$$

the energy contained within a range $d\mu$ becomes proportional to

$$\frac{1}{\kappa} e^{-a^2\kappa^2} d\mu\,;$$

the factor of $d\mu$ being infinite for infinite values of the wave-length. This puts Weber's law out of court. We may, however, draw this conclusion from it :—If a is taken to be infinitely large all radiations are of equal intensities. In that case the excess of energy which we have deduced from the law vanishes at every point, and the two sources may be said not to interfere with each other.

As an approximately correct law for the distribution of energy in the spectrum we may take that suggested by Michelson, and write for the energy $S d\kappa$, where

$$S = C\kappa^4 e^{-a^2\kappa^2}.$$

The excess of energy according to (5) will be proportional to

$$\int_0^\infty \kappa^4 e^{-a^2\kappa^2} \cos 2\kappa\tau \, d\kappa = \frac{\sqrt{\pi}}{8a^9} e^{-\tau^2/a^2}(4\tau^4 + 3a^4 - 12a^2\tau^2).$$

If we call $E_0 \, dx$ the energy supplied to a strip of width dx and unit length by each source separately, then for $\tau = 0$ the energy should be $4E_0 \, dx$. Hence the excess of energy $(E - 2E_0)$ due to the double source will be determined by

$$E - 2E_0 = \frac{2}{3} E_0 e^{-z^2}(4z^4 + 3 - 12z^2), \quad . \quad . \quad . \quad (6)$$

where z is written for τ/a.

The retardation τ may be expressed in the usual way in terms of the distance of the two sources from each other and from the screen. If

D = distance of screen from source of light;
$2d$ = distance of the two sources of light from each other;
V = velocity of light;
x = distance of any point of the screen from the central line, *i. e.* that line on the screen for which $\tau = 0$;

we have the following relations :—

$$\tau = xd/(VD),$$
$$z = xd/(VDa).$$

The quantity a can be determined if we know the wave-length for which the energy is a maximum in a spectrum formed by a grating, the condition for the maximum being

$$\frac{d}{d\kappa}\left(\kappa^6 e^{-a^2\kappa^2}\right) = 0,$$

or

$$\kappa a = \sqrt{3}.$$

Hence

$$\lambda_{(\text{max.})} = \frac{2}{\sqrt{3}} \pi a V.$$

As we are now dealing with the only interference-effect which can properly be said to take place with white light when the source is only doubled, and not multiplied more frequently as in the case of thin films, it seems worth while to discuss the energy-curve as given by (6) a little more closely.

In fig. 7 (page 541) the line A gives the assumed illumination of the screen due to the source only. The source being doubled by the introduction of the mirror, the straight line B gives on the same scale the illumination of the screen calculated on the assumption that there is no interference; the intensity in that case being simply doubled. The curve C gives the actual illumination obtained by Lloyd's mirror-arrangement, calculated on the hypothesis that Michelson's formula for the

distribution of energy in the spectrum is correct. The difference between the ordinates of B and the curve C may be taken to measure the amount of interference. The curve D gives the assumed distribution of energy in the grating-spectrum, the abscissæ being wave-lengths drawn to such a scale that a particular value of the wave-length is placed at that point of the screen at which the corresponding homogeneous radiation would have its first principal maximum. Analytically the curves are represented (y and z being the ordinates and abscissæ) by the equations

$$y = 2 + \tfrac{2}{3} e^{-z^2}(4z^4 + 3 - 12z^2), \quad . \quad . \quad . \quad . \quad \text{(C)}$$

$$y = \frac{1}{z^6} e^{-\pi^2/z^2}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(D)}$$

Assuming the illumination due to the one source alone to be E_0, the principal features of the curve C are :—

(1) At the intersection of the screen and mirror the illumination is $4E_0$.

(2) The intensity diminishes until a value of z is reached for which $z^2 = \tfrac{3}{2} - \sqrt{\tfrac{3}{2}} = \cdot275$ (or $z = \cdot524$). The total energy is then $2E_0$, and at this point we may say that no interference takes place.

(3) The intensity diminishes still further, and now becomes less than that due to the sum of the two separate sources. The minimum intensity takes place when

$$z^2 = \tfrac{5}{2} - \sqrt{\tfrac{5}{2}} = 0\cdot919 \ (z = 0\cdot959).$$

The value of E_0 at this point becomes $0\cdot78\,E_0$, or only about three quarters of the energy due to each source alone.

(4) The intensity increases again, and at a point for which $z^2 = \tfrac{3}{2} + \sqrt{\tfrac{3}{2}} = 2\cdot725$ ($z = 1\cdot65$) it is once more equal to $2E_0$.

(5) A maximum of intensity takes place when

$$z^2 = \tfrac{5}{2} + \sqrt{\tfrac{5}{2}} = 4\cdot081 \ (z = 2\cdot02).$$

The maximum is not very pronounced, its value being $2\cdot24\,E_0$.

(6) The intensity diminishes and gradually approaches the value $2E_0$. The total excess of energy on the screen vanishes as

$$\int_0^\infty e^{-z^2}(4z^4 + 3 - 12z^2)\,dz = 0.$$

As a result of our calculation, we may say that in all cases where interference is produced by an artificial doubling of the source, such as in Fresnel's mirrors or biprisms, or in Lloyd's mirror-arrangement, the true interference-curve with

white light does not consist of alternate bright and dark
bands, but is represented by the curve C (fig. 7), and has only
one well-defined minimum.   There would be no interference
at all, in the sense the word is used here, if we could have a
source of light giving out all radiations with equal intensities.
If we can draw a curve such as that given, it is only because
we know that the energy of our available sources of white
light is distributed in a way which cannot differ much from
that represented by the curve D (fig. 7).   There would be no
difficulty in extending our investigation to the case of thin
films and other cases in which the source of light is multi-
plied more than twice.   The general result, however, would
not be altered ; whatever interference there is, must depend
on the prevalence of some particular wave-length in the
original spectrum.

20. Imagine, now, a photographic film to be substituted
for the screen in the last section.   The curve C (fig. 7) would
evidently not represent the effect on the film, for the bands
commonly associated with interference-effects would appear ;
this indicates an interference phenomenon which is not in-
cluded in the cases we have hitherto discussed.   To explain
how the photographic film can *produce* interference where
it previously did not exist, we may think of a pendulum
which is set in motion by a blow and moves without fric-
tion.   Suppose that after a certain lapse of time the blow
is repeated.   The second blow may increase or diminish
the momentum due to the first blow according to the rela-
tion between the interval of time which intervenes between
the blow and the time of vibration.   It will be quite con-
sistent with our use of the word if we say that the second
blow has "interfered" with the first.   But if friction be
introduced so that, before the second blow is delivered, the
motion due to the first has practically died out, the second
blow will produce its own effect whatever the interval of time
between the blows.   There is now no interference, and the
interference in the previous case is seen to depend on the fact
that the effect of the first blow is a periodic motion continued
for a sufficient number of periods.   From the case of a single
blow we may proceed to the discussion of impulses delivered
at regular intervals.

Consider two exactly equal pendulums vibrating in a
period t.   Let blows be delivered to the first at regular
intervals t, and to the second at intervals $t + \tau$.   If n blows
have been delivered, the first being given simultaneously in
both cases, the blows given to the second pendulum will be
behind those given to the first by an interval $n\tau$.   If that

quantity is not more than a certain fraction of a period, which we may roughly take to be a tenth, the energy gained is practically the same in both cases. But as n increases, the first pendulum will gradually accumulate an amount of energy decidedly greater than the second, provided there is no friction. If the friction is sufficiently large so that in the interval $n\tau$, at which the non-agreement of phase between the blows and the pendulum comes to be important, the effects of a single blow are practically obliterated, the two pendulums will show no appreciable difference in energy, whatever the time. If, on the other hand, not knowing beforehand whether there is any friction or not, we observe that the two sets of blows delivered at intervals t and $t + \tau$ produce a markedly different effect on the pendulum, we may fix a lower limit to the possible amount of friction that can exist, and may say that a single blow must produce an effect which lasts through a number n of periods, where the value of n must be greater than that at which the difference in phase becomes detrimental.

From the effects produced by a succession of blows we may pass to those produced by a continuous periodic force. A vibrating system without friction, whose natural period is $2\pi/n$, will, if acted on from rest by a force $E \cos \kappa t$, show a displacement

$$\alpha = \frac{E}{n^2 - \kappa^2} (\cos \kappa t - \cos n t),$$

$$= \frac{2E}{n^2 - \kappa^2} \sin \left(\frac{n + \kappa}{2} \right) t \sin \left(\frac{n - \kappa}{2} \right) t.$$

The latter form of the equation shows that if n and κ are nearly equal, the motion is approximately represented by a vibration of amplitude $\frac{2E}{n^2 - \kappa^2} \sin \frac{n - \kappa}{2} t$, the maximum velocity being

$$u = \frac{E}{n - \kappa} \sin \frac{n - \kappa}{2} t = E \left(\frac{t}{2} - \frac{(n - \kappa)^2 t^3}{48} \right),$$

if $(n - \kappa)t$ is sufficiently small. If u_0 is the maximum velocity in the special case that $n = \kappa$,

$$\frac{u_0 - u}{u_0} = \frac{(n - \kappa)^2 t^2}{24}.$$

Supposing we are dealing with luminous vibrations, and that our eye can easily appreciate a difference of intensity of 2 per cent., that is a difference in amplitude of 1 per cent., we find that the time t at which we begin to draw a clear

distinction between the effects of the force $E \cos \kappa t$ and $E \cos nt$ is given by

$$(n - \kappa)t = \tfrac{1}{2} \text{ nearly.}$$

This means that the difference in phase between the forces at the time t may amount to nearly 30°. If we introduce the periodic times of vibration of the two forces $T_1 = 2\pi/n$ and $T_2 = 2\pi/\kappa$, we may say that, in order that they should introduce a difference in the energy amounting to two per cent. of a vibrating system whose natural period is $2\pi/n$, it is necessary that they should continue to act for m vibrations where

$$\frac{m(T_2 - T_1)}{T_1} = \frac{1}{2\pi} \sqrt{\cdot 24} = \cdot 08 \text{ approximately.}$$

If the vibrating system is subject to friction, and the difference in the energy absorbed is two per cent., it follows that the friction must be sufficiently small to allow a single impulse to produce vibrations which do not appreciably diminish in m vibrations, where m is the number determined by the above equation.

All these considerations tend to show that if a medium absorbs strongly some particular wave-length and transmits another wave-length near it, the particles must be capable of being set into vibration by an impulse, and that the periodic disturbance of the particle produced by the impulse must last the longer, the more sudden the variation in the coefficient of absorption. The fact that a substance draws a distinction between two periods in the incident light which are near together implies a regularity of vibration in the substance capable of being produced by irregular impulses of the medium.

If we produce an interference-pattern on a photographic screen, and by this means are able to observe interference with large difference of path, the case is exactly analogous to that in which a grating or prism is used. The regularity which enables us to observe the interference lies in the instrument of investigation, and does not prove anything with respect to the regularity of white light. Our eye is an instrument which distinguishes light of different wave-lengths; this implies a certain regularity in the motion produced by an impulsive disturbance of the medium. If an impulse reaching the retina did not call forth periodic motion in nerve-fibres persisting for some appreciable time, the interference-spectra observed, say, with Lloyd's mirror would be identical with that indicated by a thermopile, as shown in fig. 7. But we see a succession of a few spectra, and may gain a rough idea of the number of periods

during which a more or less regular motion is produced in our eye by the action of light. We may easily distinguish

Fig. 7.
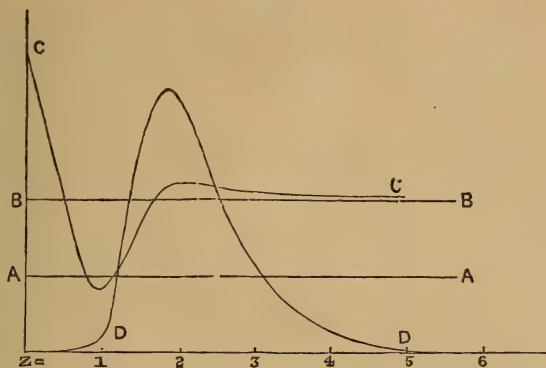
between yellow and orange light, the periodic times of which stand in the ratio of 61 to 59. The fraction $(T_2 - T_1)/T_1$ is about $\frac{1}{30}$, and the number of vibrations during which the effects of an impulse will last must at least contain 24 complete periods. On the other hand, I think we should find it difficult to distinguish in any part of the spectrum between two vibrations the periods of which differ by the three-hundredth part of either; and we may conclude that the *physical* effects of an impulse in the eye could not show any regularity lasting for much more than 300 periods. We are not of course dealing here with the physiological actions which prolong the sensation of light for a measurable time.

The fact that white light shows any objective interference at all, without the artificial introduction of regularity, is due to the prevalence of certain wave-lengths over others. Whatever regularity there is in the light is intimately connected with the distribution of intensity in the spectrum.

We cannot help speculating as to the ultimate cause which renders the regularity of vibration a function of the temperature only, and independent of the natural periods of the molecules. Perhaps the solution of the difficulty will be found in the fact that our observations tell us nothing directly as to the vibrations of the atoms or molecules. What we observe is the disturbance of the medium, and the distribution of energy in the spectrum of an incandescent black body which is in thermal equilibrium may indicate a property of the medium rather than that of matter. That is to say, the motion of vibration in the molecule may be perfectly

irregular, but the medium may take up and propagate some vibrations quicker than others.

There are many signs tending to show that the time is not far distant when, in order to explain the connexion between optical and electrical facts, we must recognize some structural properties of the medium, and the regularity in the vibration of a black body may be intimately connected with such structural properties.

21. The result of this paper is in complete agreement with the conclusions formed by Gouy and Lord Rayleigh as to the nature of white light. We have obtained an expression (§ 8) for the disturbance produced by a grating if the disturbance in the incident light is given, and traced the result in special cases. We have more especially examined the case in which bright and dark bands are formed in a spectroscope when two sets of rays are brought to interference, one having a certain retardation compared to the other, and shown (§ 14) that provided the intensity of light does not sensibly vary from one band to the next, the relative intensity of the maxima and minima can be given in terms of the retardation and resolving power without any hypothesis as to the nature of light. No conclusions, therefore, can be drawn as to the "regularity" of white light. The nature of light, including its "regularity," as follows from Rayleigh's investigations, is completely defined by the distribution of energy in the spectrum.

The analysis of the spectrum by a prism is shown (§ 15) to involve, like that of a grating, the spreading out of an impulse over a length of time which increases with the resolving power. That is to say, a single impulse falling on the slit of the collimator will not pass through the focal plane of the telescope as a single impulse, but as an oscillatory motion. This follows in a simple manner if we consider the passage through a prism of a "group" of waves, the front of which moves with the group velocity.

In § 18 an expression has been obtained for the distribution of light on a screen, in a case of simple interference like that of Lloyd's mirror arrangement. The expression again only involves the distribution of energy in the spectrum. If all wave-lengths were equally represented, there would be no interference at all. The coloured bands which are *seen* in this case, as well as the colours of thin films, are shown, § 20, to be due to interference produced in the eye itself, and to depend on the fact that in any substance showing selective absorption a single impulse produces an oscillatory motion lasting for some time. In order that two impulses should

interfere, it is necessary that their effects should overlap. When an interference pattern is produced either in a spectroscope, or with the help of a medium like the eye showing selective absorption, it always means that each impulse is spread out so as to overlap the one which follows. Looked at from a different point of view, we may say that *two* periodicities are involved in every case of interference. We have, in the first place, a retardation of path of the two interfering rays. Whatever the nature of light, if analysed by Fourier's theorem, this retardation is seen to produce a periodicity, which, however, alone is not sufficient to give rise to interference effect. The prism or grating which analyses the light, or some medium showing selective absorption, introduces the second period. If there is without such means an interference which can be objectively observed with a thermopile or bolometer, it means that there must be some prevailing period in the original light. The light may be homogeneous or it may only show like sunlight a maximum of intensity in some region of the spectrum.

22. We have calculated the disturbance produced by a grating with the help of an equation (1) § 8, which may be proved in a more rigorous manner. Let ϕ be a function satisfying the differential equation

$$\frac{d^2\phi}{dt^2} = a^2\nabla^2\phi, \quad \ldots \ldots \quad (7)$$

and having given values ϕ and $\frac{d\phi}{dn}$ at the boundaries of the space we are considering. Kirchhoff[*] has shown that at any point P within that space $\phi(t)$ may be expressed by

$$4\pi\phi(t) = \int\Omega dS,$$

where the integration is extended over the boundary of the space, and

$$\Omega = \frac{d}{dN}\frac{\phi\left(t - \frac{r}{a}\right)}{r} - \frac{f\left(t - \frac{r}{a}\right)}{r},$$

$$f(t) = \frac{d\phi}{dN}.$$

N is the normal directed to the inside of the space, and r is the distance of the point P from the element dS of the surface. The differentiation in the first term of Ω is to be carried out as if r were the only variable. The expression

[*] " Zur Theorie der Lichtstrahlen," Wied. *Ann.* Bd. xviii. p. 663 (1883), and *Gesammelte Abhandlungen*, Nachtrag, p. 22.

can be simplified if the only part of the boundary at which ϕ does not vanish consists of a plane surface. Write

$$2\pi\psi_1 = \int \frac{d}{d\mathrm{N}} \frac{\phi\left(t-\frac{r}{a}\right)}{r}\, d\mathrm{S},$$

$$-2\pi\psi_2 = \int \frac{f\left(t-\frac{r}{a}\right)}{r}\, d\mathrm{S},$$

so that

$$2\phi = \psi_1 + \psi_2. \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

Both ψ_1 and ψ_2 satisfy separately the differential equation (7).

The value of ψ_1 at a given point and time is expressed as the potential due to a double layer. Of such a potential it is known that it shows a discontinuity at the surface equal to $2\phi(t)$. Hence if the surface is plane the ψ_1 at the surface must be equal to $\phi(t)$. The function ψ_1 takes, therefore, the same value as ϕ at the surface, and from (8) it follows that the same must hold for ψ_2 also.

The value of ψ_2 is expressed as a surface potential, and the form of the integral shows that at the plane surface

$$\frac{d\psi_2}{d\mathrm{N}} = f(t) = \frac{d\phi}{d\mathrm{N}}.$$

Hence the differential coefficient of ψ_2 at the surface is the same as that of ϕ, and it follows again from (8) that the same must also hold for ψ_1.

Both ψ_1 and ψ_2 satisfy, therefore, all conditions: hence, taking as axis of z the direction of the normal, we may, for the special case under consideration, write Kirchhoff's equation

$$2\pi\phi(t) = \int \frac{d}{dz} \frac{\phi\left(t-\frac{r}{a}\right)}{r}\, d\mathrm{S},$$

$$= \frac{d}{dz} \int \frac{\phi\left(t-\frac{r}{a}\right)}{r}\, d\mathrm{S},$$

$$= -\int \frac{f\left(t-\frac{r}{a}\right)}{r}\, d\mathrm{S},$$

all of which forms may be useful. Taking the first, performing the differentiation, and rejecting the terms which vary

inversely as the squares of the distance compared to those terms which alone are of importance, unless the point under consideration is close to the surface, we find

$$2\pi\phi(t) = \int \frac{1}{r} \cdot \frac{d}{dz} \phi\left(t - \frac{r}{a}\right) dS = -\int \frac{1}{ar} \cdot \frac{dr}{dz} \frac{d}{dt} \phi\left(t - \frac{r}{a}\right) dS.$$

To apply this equation to the special case treated in § 8 we take ϕ at the surface to be independent of that direction which is parallel to the lines of the grating and measure s at right angles to the lines; if $2l$ is the width of the grating, h its length, r_0 the value of r for that line which is drawn from any point P to the centre of the grating, β the angle between r_0 and the normal, and if finally r_0 is taken to be very large,

$$2\pi\phi(t) = \frac{h\cos\beta}{ar_0} \int_{-l}^{+l} \frac{d}{dt} \phi\left(t - \frac{s}{a}\sin\beta\right) ds.$$

The amplitude of the disturbance at the focal plane of a telescope varies inversely with the focal length; hence, if instead of receiving the light on a screen at an infinite distance, we collect it by means of a lens of focal length F, we must substitute F for r_0 in the above expression. Let now $\psi\left(t - \dfrac{x}{a}\right)$ be the disturbance in the incident beam which falls on the grating at an angle α, and let, as in § 8, the grating act in such a way as to reduce ψ in the ratio $\cos qs$. The value of ϕ at the grating will for the reflected beam become

$$\phi(t) = \cos qs \cdot \psi\left(t + \frac{s\sin\alpha}{a}\right),$$

and if we put $\gamma = s(\sin\beta - \sin\alpha)$,

$$2\pi\phi(t) = \frac{h\cos\beta}{aF} \int_{-l}^{+l} \cos qs \frac{d}{dt} \psi(t - \gamma s/a) ds.$$

This is the equation we have made use of for the displacement produced at the focus of a lens, of focal length F, by a simple grating the lines of which are at a distance $2\pi/q$, the displacement in the incident beam being given as $\psi(t - x/a)$.

LIII. *A New Mode of making Magic Mirrors.*
By J. W. Kearton*.

THE first explanation that occurred to me on seeing the Japanese mirror about fourteen months ago was that the face might bear directly invisible differences in polish, which a powerful beam of light would probably convert into visible ones by reflexion on to the screen. To produce such minute differences, it was my intention to take pairs of different metals closely agreeing in colour and reflective power, as silver and platinum, and to deposit electrically in the form of some easily recognizable figure a thin coating of the one metal on a groundwork of the other. Very faint mercuric staining of bright metallic surfaces was also contemplated. These ideas, however, resolved themselves into a test much simpler, yet involving the same principle. A piece of metal was so polished that in subdued daylight a cross, more finely burnished than the general surface of the plate, could just be distinguished. Reflected on to the screen, the figure came out exceedingly faint; and this fact, apart from the consideration that figures so produced could have only a precarious existence, was sufficient to condemn the hypothesis in question.

This result has a bearing upon another hypothesis—one worthy of prompt burial with the quiddities and essences of the purely deductive method, viz., that the magic-mirror phenomena are due to local molecular rearrangements in the reflecting surface, brought about by unequal cooling of the mass of the mirror. Now, since it is held that the regularity or convexity of the surface is not thereby affected, this molecular rearrangement can put itself in evidence optically only by reflecting more or less light than the parts of the surface unaffected by irregular cooling. But it has been shown that with figures so pronounced as to be directly visible, the electric beam is powerless to produce results comparable in intensity with those given by the Japanese mirror; much less will directly invisible figures of the type under reference come up to the required standard.

The plate used in the foregoing experiment, whilst furnishing no clue in virtue of its polished figure, yet presented evidence that pointed clearly in the direction where a solution of the problem was to be found. Strikingly well-defined lines and dapplings of light were thrown on the screen by

light reflected from the disk. These marks were found to correspond to concave strains produced by hammering the plate into rough convexity before scouring down with charcoal. Depressions produced by electro-deposition of silver on a silvered plate, protected in parts by varnish according to the figure desired, were therefore tried ; but they invariably deepened into the underlying brass before the sharp edges of the figure were polished away.

Next, a fairly thick coating of silver was deposited on the plate, and a pointed bit of agate was repeatedly drawn with pressure over certain parts of the porous layer of metal. The figures thus obtained were startling ; for the depressions appeared on the screen as reticulated lines of deep shade, which had their analogue in the broken spinal divisions left by the agate point. The bad working of metals electrically deposited caused me to give up the deposition method.

My plate of brass was next slung up in a weak solution of copper sulphate and sulphuric acid on the positive wire of a pint bichromate-cell. After an immersion of four minutes, the parts of the plate not protected by the naphthaline solution of sealing-wax came out beautifully fretted. After several attempts on these lines, and two days after the lecture delivered here by Prof. S. P. Thompson on the 27th of January last on the Magic Mirror, my first success was achieved in the shape of a mirror 2 inches in diameter, representing a stem with leaves and a guide-post standing in a mound of earth. From that mirror to my present one, the first of the new class being completed in the following July, was, however, a far cry. Applied to larger mirrors and figures, the electrical method proved essentially bad. Exactly contrary to what was required, the figures were deeper at the edges of the lines than at the central parts : indeed, a broad line scoured down into two lines defining the lateral limits of the original one.

Nitric acid was finally adopted as the figure-eating agent, care being taken to use good brass and to polish well before immersion, so that the action on the plate might be uniform. Smooth figures were thus produced after immersions of upwards of six seconds in strong acid. The walls of the figures are perpendicular to the surface of the disk, and the determination of their proper height relatively to the breadth of the lines of the figure involved much further labour. The process of scouring with Sheffield lime and swans'-down calico has a double effect—it rounds off the upper rectangular edges of the walls, and at the same time converts the flat floors of the figure into concave depressions, the walls and

floors finally merging into one concave sweep. This curve, with narrow lines, is sharper than with broad lines; consequently the latter may disappear, while the former remain visible. Very brief immersions in the acid are therefore not suitable for figures having lines differing much in breadth. Long immersions, on the other hand, are objectionable both on the ground of the excessive labour in rounding off the edges, and of the well-nigh impossible task of reducing uniformly the deep runnels of the figure by scouring the general surface with charcoal.

Gradations in depth according to the breadth of the several limbs were therefore tried, and produced in the following way :—The figure, say of a tree, is made by removing paraffin wax from the brass plate with a pointed stick of boxwood, and is then fixed by a very short immersion in the acid. The slender branches are now painted over with hot wax, and the broader branches and trunk are reduced in breadth symmetrically by the same means, the plate then being immersed a second time. By a repetition of alternate painting and immersing, all the members of the figure are made to increase in depth by fine gradations from the boundary lines to the central parts. This method, specially applicable to figures with very broad and narrow lines, is, however, rather troublesome, and does not give satisfactory results unless the gradations are minute, which otherwise will be brought out by reflexion on to the screen.

Reverting to single immersions, final experiments were made with plates bearing figures prepared in the usual way, viz. by removal of wax, a record being kept of the strength of the acid and the time of immersion in each case. The result is that for figures with lines ranging from $\frac{1}{16}$ to $\frac{3}{8}$ of an inch in breadth, an immersion of 3 seconds in a solution of 5 volumes of concentrated nitric acid to 2 of water gives a satisfactory depth.

The next step was to produce figures in low relief, which come out on the screen in shade. As there is in this case no intersection of the reflected rays, and, consequently, no blotting out or dimming of the figures, very narrow lines may be used. These are conveniently drawn with a camel's-hair brush and sealing-wax dissolved in naphtha. From 1 to 2 seconds' immersion, according to the breadth of the characters, will be found sufficient.

LIV. *The Minimum Temperature of Visibility.* By P. L.
Gray, *B.Sc., Assoc. R.C.S., Lecturer in Physics, Mason
College, Birmingham*[*].

THE title of this paper is, for convenience, somewhat
elliptical. Fully, it should be "The Minimum Tem-
perature at which·a Strip of Platinum, either bright or lamp-
blacked, becomes visible in the dark."

Apparently no exact work has been done on the point since
that of Draper ("On the Production of Light by Heat," Phil.
Mag. 1847, xxx. p. 345), who used a somewhat similar method
to that described in this paper. This work seems to be gene-
rally little known, vague statements, usually without authority,
being given when the subject is referred to at all. It only
fell under the present writer's notice after the observations,
detailed below, had been completed.

Draper looked at a small strip of platinum, only $\frac{1}{20}$ inch
wide, in a dark room, gradually heating the metal by an
electric current until it became visible, and estimating its
temperature from its linear expansion, measured by a mag-
nifying-lever method. Taking a mean coefficient of expansion,
from Dulong and Petit's results, with a lengthening of $\frac{1}{222}$,
he arrives at a temperature of 525° C. This is obviously too
high, as no account is taken of the increase of the coefficient
with temperature. Taking the most recent result[†] for pla-
tinum,

$$\alpha = 10^{-9}(8901 + 1\cdot21\,t),$$

or

$$\frac{dl}{dt} = 10^{-9}(8901 + 1\cdot21\,t)\,;$$

and integrating, we have

$$l_t - l_0 = 10^{-9} \times 8901\,t + 10^{-9} \times 1\cdot21\frac{t^2}{2},$$

or

$$\frac{1}{222} = \cdot0045045 = \qquad ,, \qquad ,, \qquad ,,$$

whence $t = 490°$ C.

As this formula was only tested experimentally up to about
73° C., it is most likely that another term, in t^2, should be
added, which would somewhat reduce this value, and thus
produce a satisfactory agreement between Draper's result and
the maximum obtained by myself.

In the same paper Draper arrives at the conclusion that *all solid bodies become visible at the same temperature*; a conclusion which is fully borne out by the observations given below, as to the equality of temperatures in the case of bare and lamp-blacked platinum.

Draper's value being, as shown above, somewhat doubtful, the point seems worthy of more exact experiment, both from a physical and a physiological point of view ; and as I had, in beginning a series of investigations on Radiation, a means of keeping a platinum surface at any desired temperature, I made a number of observations on the subject, while waiting for other apparatus for use with which the platinum strip was primarily intended.

The instrument in question is Wilson and Gray's modified form of Joly's Meldometer, and is described in their paper, "Experimental Investigations on the Effective Temperature of the Sun," read before the Royal Society on March 15th, and shortly to be published*. It consists essentially of a strip of very thin platinum, about 10 centim. long, 1 centim. broad, and $\frac{1}{50}$ millim. thick. The plane of the strip is vertical.

It can be heated by an electric current, and its linear expansion is indicated by an optical method, by which an alteration in temperature of 1° can easily be noticed. The method of calibration is described in Joly's paper †, and in that already mentioned, so that it is unnecessary to do more than briefly refer to it here. Minute fragments of substances of known melting-points are placed on the strip and watched through a microscope, while the temperature is very slowly and cautiously raised until, in any case, melting is seen to take place, when the position of the spot of light which indicates the expansion of the strip is noted. In these experiments the substances used were K_2NO_3 (339°), AgCl (451°), KBr (699°), and gold (1041°) ‡. From these observations a curve showing the relation between temperature and scale-readings is obtained. One point may, however, be mentioned, viz. as to the difference of temperature between the middle of the strip and its surface. Joly says § that the difference is probably measured by hundredths of a degree only. The following figures will show the correctness of this assumption.

At a temperature of about 500° C., amount of energy lost per second per square centimetre = ·3 calorie.

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* Phil. Trans. 1894.
† Proc. R. I. A. vol. ii. 3rd series, 1891–92, p. 38.
‡ See the same two papers already quoted.
§ Proc. R. I. A. vol. ii. 3rd series, 1891–92, p. 49.

Thickness of section $=\frac{1}{50}$ millim. $=\cdot002$ centim.

$\therefore$ Half ,, ,, $=$ $\cdot001$,,

Flow of heat $=\dfrac{k\theta}{d}$, where $k=$ conductivity $(=\cdot2)$, and $\theta=$ the difference of temperature required, at the ends of the distance $d\ (=\cdot001$ centim.$)$,

$$\therefore\ \cdot3=\frac{\cdot2\theta}{\cdot001},\quad\text{whence }\theta=0^{\circ}\cdot0015.$$

The loss of energy per unit area was obtained by a voltmeter-and-ammeter method, which is to be further developed for the Radiation experiments. All the figures are approximate, the smallness of the resulting difference (about $\frac{1}{1000}^{\circ}$ C.) showing that there is here no need for any high degree of accuracy.

With the surface of the platinum lampblacked the case is different; but even here an approximate calculation shows that there is still less than 1° difference between the platinum and the surface of the carbon. In a typical case the following results were found:—

Thickness of layer $=\cdot00033$ centim. This was determined from a knowledge of the specific gravity of the lampblack.

Conductivity $=\cdot0002$. This is the value given by Everett for powdered carbon, and is probably *less* than the correct value for the lampblack; but the two must be of about the same order of magnitude.

Loss of heat per unit area at 500° C. $=\cdot5$ calorie per second;

$$\therefore\ \cdot5=\frac{\cdot0002\,\theta}{\cdot00033};\quad\therefore\ \theta=0^{\circ}\cdot8.$$

Method of Making the Experiments.

The first requisite was to get the strip in a perfectly dark enclosure, within which both eyes could be directed towards it without strain. To this end the apparatus was enclosed in a wooden box (blackened within), one end of which was replaced by a black velvet cloth, under which the observer placed his head, and which he could gather round his neck and under his chin so that not a ray of light could penetrate the enclosure. The box was about 48 centim. long, 30 broad, and 22 high, and ordinarily the eyes, in making an observation, would be about 30 centim. from the strip. The other end of the box was provided with a hinged shutter, which was lifted immediately after an observation had been made, for the purpose of noting the temperature of the strip.

The strip itself was further protected from draughts &c. by means of a piece of brass, bent twice at right angles, and

resting on the slate block below the strip, as in the calibration experiments ; thus (natural size) :—
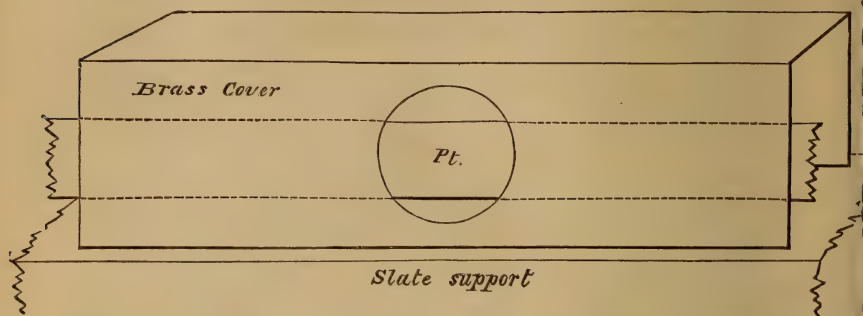
The angular dimensions of the surface of platinum, as seen in any experiment, were therefore :—

Apparent length $= 3° 49'$ approximately ;
  „   width $= 1° 54'$ „

so that the apparent area subtended was about 36 times that of the full moon.

The current by which the strip was heated ran through a variable carbon resistance, the handle of which was within convenient reach of the observer as he sat with his head under the black cloth. He could thus alter the temperature of the platinum until it was on the very verge of invisibility, a very small fraction of a turn being then sufficient to produce utter darkness where before the area of faint light had been. A contact-breaker was also within convenient reach, so that the current could be broken or made at pleasure, and the objective reality of the faint luminosity at the limiting-point thus demonstrated. When he was satisfied that the limiting-point had been reached the hinged end of the box was opened, a beam of light sent to the mirror connected with the strip, and the deflexion, giving the temperature, read on the scale. The possible error in the estimation of the absolute value of the temperature may be taken as certainly not more than $2°$.

Discussion of the Results.

My first idea, in putting down final results, was to take the mean of a large number of observations as expressing the required minimum temperature ; but there soon appeared to be too much variation in individual cases, both for the same eyes at different times and for different people's eyes, for this mean to be of any value. It seems better, therefore, to put down the determinations in some detail, with such remarks as may help towards some general conclusions afterwards.

The first case given is my own, in which it has naturally been easier to obtain a larger number of records than in the case of other people.

The dates are given merely to distinguish one day's observations from another's.

The letter B after any temperature signifies that the surface was lampblacked in that experiment; otherwise it was bare, and in its ordinary condition of polish.

The details of the observations are as follows :—

Feb. 10th. 451°, 460°, 460°, 444°, 447°, 448°. Observations made in the morning, without any special preparation as to resting the eyes.

„ 14th. 427°, 422°, 422°. Evening.

„ 15th. 437°(B), 432°(B), 427°(B), 427°, 427°. Evening.

„ 16th. 422°, 418°, 421°, 419°(B), 419°(B). Evening; 2nd observation after two minutes in complete darkness.

„ 19th. 410°, 410°. Evening.

„ 22nd. 409°, 409°, 408°. Evening.

After these observations more attention was paid to the time of day and the state of preparation of the eyes.

Feb. 26th. 401°, 397°; 388°, 394°, 384°; 398°, 403°. Evening. Between 2nd and 3rd observations, 11 minutes were passed in perfect darkness; after the 5th, 10 minutes in writing under a bright incandescent lamp.

Before the next set, 16 minutes with eyes shut in nearly dark room :—

383°, 392°, 392°(B), 409°(B), 409°(B), 416°, 417°, 409°.

„ 27th. 470°, 464°, 461°, 463°. Morning (bright).

413°, 414°; 392°, 400°, 400°; 410°. Evening; 3rd observation after half an hour with eyes shut. Several more observations were made, showing a regular fall of temperature after resting the eyes in the dark, and a rise after reading &c., the limits being about 390° and 410°.

„ 28th. 455°, 447°, 447°; 459°. Morning (dull).

„ „ 453°; 417°, 415°, 419°. Afternoon; 4 minutes in darkness after 1st observation.

„ „ 407°; 389°, 389°; 404°, 399°; 392, 392°, 393°. 16 minutes in darkness between 1st and 2nd observations; 12 minutes' reading between 3rd and 4th, and again a few minutes' rest after the 5th.

Observations on two succeeding days gave readings varying from 470° in the morning to 385° in the evening, the influence of rest in darkness being always plainly marked.

To test if the intervals of rest noted above were sufficient to bring the eyes to their extreme state of sensitiveness, some observations were made at 3 A.M., after I had been asleep in a dark room for 3 hours. The readings then obtained were 373°, 386°, showing a slightly greater sensitiveness than that in any previous experiment; the small difference probably indicates that the eyes were very near their extreme limit, and that no longer rest would give a lower reading.

Before going on to the general conclusions to be drawn from these results, the values are given obtained by other observers, who (with the exception of two) were either members of the staff, or students, of Mason College. They are probably not equally trustworthy, and in general no particular preparation was gone through by the observer.

Usually the first observation in each case showed a higher temperature than the second and succeeding ones. This was to be expected, since the time spent in darkness during the first experiment prepares the eye to a certain extent for the second. The results obtained are as follows :—

		Case A.	Mean temperature		. .	432° C.
,,	B.		,,	,,	. .	422
,,	C.		,,	,,	. .	436
,,	D.		,,	,,	. .	409
,,	E.		,,	,,	. .	428
,,	F.		,,	,,	. .	438
,,	I.		,,	,,	. .	426
,,	J.		,,	,,	. .	440

All the above were taken either in the morning or early in the afternoon.

Case H.   Mean temperature   . .   408°.

In this case the room was darkish.

Case G.	Evening	. . . . .	388°
	Morning	. . . . .	435°
	Evening	. . . . .	380°–385°

The last observation was made after 17 minutes had been spent by the observer with his eyes shut in the nearly dark laboratory.

General Conclusions.

(1) *That the minimum temperature of visibility is the same for a bright polished metallic surface as for one covered with lampblack,* although the intensity of the radiation in the two cases may be different.

This result may at first be, to some, unexpected, but a little consideration will show that it might have been, *à priori*, anticipated. For probably temperature governs the highest wave-length from a radiating body, and wave-length governs visibility, at least after an extremely small intensity of radiation has been passed *.

(2) *That the visible limit at the red end of the spectrum varies greatly for a normal eye, according to its state of preparation*; *i.e.* according to the intensity of the light in which the observer has been before making the observation.

I take my own eyes as normal; they have been tested in the Anthropometrical Laboratory at S. Kensington, and roughly by Captain Abney's method; and in the figures given above the results are supported by those obtained by the other "cases," none of whom† are known to have abnormal sight.

Speaking generally, we may say that a bright light diminishes the sensitiveness of the eye to radiation of low frequency; that darkness increases it. Or that, as a rule, the eye is less sensitive in the morning than at night.

(3) *That for the less sensitive condition, the minimum temperature of visibility for the surface of a solid is about 470° C., but that this may be much reduced by even a few minutes in a dark room.*

(4) *That at night, a surface at a temperature of 410° is visible, and that by resting the eyes in complete darkness, this may be reduced to as low as 370° nearly, below which apparently one cannot go,* since 10 minutes' rest appears to be almost as efficacious as 3 hours'.

(5) *That different people's eyes (of no special or known departure from normality) differ somewhat in their "minimum temperature of visibility," but probably not to any great extent, if tested under the same conditions as to preparation, &c.*

Case G was a somewhat curious one; the observer was the one exception among those I tried whose red colour-perception is perhaps not quite normal. He arrived at the lowest

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* Langley, "Energy and Vision," Phil. Mag. xxvii. (1889), shows that the amount of energy sufficient to excite vision is immensely less than that radiating from the strip in these experiments, at least in the low-red wave-lengths.

† With the possible exception of Case G.

temperature in the evening without any long rest in the darkness, and, as is seen above, 17 minutes in perfect darkness produced no alteration ; yet, in the morning, he went up to about the usual figure, so that what I had hoped to find an abnormal case turned out approximately ordinary.

The loss of distinct *colour* at the low temperatures is very striking ; the appearance to myself, and to most of the observers, has absolutely nothing of red in it, but is like a white mist—the nearest comparison I can make.

In the *morning* observations, however, when the strip disappeared at from 460° to 470°, the last appearance was distinctly reddish ; and this agrees with one observation noted at night, when after getting the visibility critical-point at about 390° C., the temperature was raised until one could declare for certain that the light looked red : it was then found to be 449°.

Of course, in all the observations, the luminous area was most distinctly seen by somewhat averting the gaze from it ; generally I found it best to look in the direction of either far upper corner of the enclosure.

As already mentioned, most of the observers pronounced the appearance at the critical-point to be that of a " whitish mist ;" one, however, thought he saw a slight " lilac tinge " in it ; and " Case G " declared it to be decidedly yellow, which is interesting, because to him a red mark on white paper (such as a pip on a card belonging to one of the red suits of a pack) appears yellow, by artificial light at night.

In one experiment a plate of glass, $\frac{1}{8}$ inch thick, and in another a layer of water, $\frac{1}{2}$ inch thick, were inserted between the strip and the eye, without making the slightest difference in the phenomenon ; showing (1) that the point where these substances begin to be more or less opaque to infra-red radiation had not been reached ; (2) that the small difference in intensity produced by their insertion had no appreciable effect. This last conclusion is far more strongly borne out by the equality of temperature in the case of the bare metallic and the black surfaces, and indicates that in all the cases it was *wave-length*, and not *intensity*, which was determinative of visibility, so disposing of the possible objection that the difference between " morning " and " evening " might be due merely to the state of enlargement of the pupil of the eye, which would naturally be more contracted at the one time than at the other, thus affecting the total amount of radiation falling on the retina. Also, if such an objection were valid, it would imply that fatigue of the muscles of the

iris produced a relatively enormous "time-lag" in following changes of luminous intensity, which we know does not exist.

There seems, in fact, to be little doubt that the difference is due to the retina itself becoming sensitive to long waves after rest, which were incapable of affecting it when it was in some way fatigued by exposure to the ordinary bright light of day.

The next and obvious step is to find the respective wave-lengths corresponding to the different temperatures. This point, however, and others, cannot be determined without some additions to the present apparatus, and will form the subject of a future paper.

LV. *New Method of Determining the Relative Affinities of certain Acids. By* M. Carey Lea *.

THIS method of measuring affinities is based on the principle that *the affinity of any acid is proportionate to the amount of base which it can retain in the presence of a strong acid selected as a standard of comparison for all acids.* The standard acid being in all cases kept exactly at the same dilution.

An example will make this clearer. Sulphuric acid is here taken as the standard, and its presence or absence in the free state is ascertained by means of the herapathite test (described in this Magazine for July 1893). For simplicity, we will suppose that the quantity taken is always a gram-molecule at a fixed rate of dilution. It is evident that two gram-molecules of sodium hydroxide would exactly saturate it. If, now, we take a given acid, we may find that a quantity of its sodium salt corresponding to three gram-molecules of sodium hydroxide will exactly extinguish the reaction of a gram-molecule of free sulphuric acid. With still another acid we may find that a quantity of its sodium salt corresponding to four gram-molecules of sodium hydroxide is needed to extinguish the sulphuric reaction. Then the affinity of the second acid is exactly twice as great as that of the first. At the point where the free sulphuric-acid reaction was extinguished, the second acid under examination retained twice as much sodium as the first, and this quite independently of any question of comparative basicity.

Throughout the series of determinations here to be described the sulphuric acid was used invariably at the same degree

of dilution, otherwise the results would not be strictly comparative. Having obtained normal acid by titration with pure sodium carbonate, this was further diluted to $\frac{N}{8}$, and 50 to 100 cub. centim. were found a convenient quantity to employ. The salt to be tested was finely powdered and thoroughly dried at 100°, or at whatever higher temperature it could support. It was then placed in a weighing-bottle and cooled in a desiccator and kept there except for a few moments at a time. By using the dry salt, the dilution of the acid was kept constant. When the point of extinguishment seemed to be reached, at least four final crystallizations were made. Great care is necessary to seize the exact point of extinguishment. The quantity of the salt found is then reduced to correspond with one gram-molecule of sulphuric acid. It is next divided by its own molecular weight : this gives the number of molecules of the salt needed to extinguish the reaction in one molecule of sulphuric acid. In order to make it possible to compare acids of different basicities, the figures thus obtained must next be modified to correspond with the basicity of the acid used. If the acid is bibasic, no change will be needed. If monobasic, the figures obtained must be divided by 2. If tribasic, they must be multiplied by $\frac{3}{2}$ &c. Finally, as the quantity characteristic of the acid is the excess of the quantity found over the amount equivalent to one molecule of sulphuric acid, unity is deducted from the amount obtained, and the residue thus found represents the comparative affinity of the acid, and may be called its *index*.

This may be rendered more clear by one or two instances.

In the case of hydrochloric acid, there was needed as a mean of many determinations 29·37 gram-molecules of sodium chloride to extinguish the reaction in one gram-molecule of sulphuric acid. At this point the solution necessarily contained

$$Na_2SO_4 + 2\ HCl + 27{\cdot}37\ NaCl.$$

This is proved beyond question by the fact that the solution no longer gives a trace of reaction of free sulphuric acid. The quantity of 27·37 gram-molecules of sodium chloride is the proportion of undecomposed sodium chloride that must remain in the solution in order that the sulphuric acid may be completely converted into sodium sulphate, and may remain as such in the solution in a condition of equilibrium.

This number 27·37 therefore represents the strength of the affinity of hydrochloric acid for sodium. But in order to compare acids of different basicities it is convenient to refer

them all to bibasic sulphuric acid, and therefore the number just found must be divided by 2. Therefore 13·68 may be taken as the index of the affinity of hydrochloric acid, in comparison with those of other acids determined in like manner.

Similarly with pyrophosphoric acid. The mean value found for the quantity necessary to extinguish the free sulphuric acid in one gram-molecule of sulphuric acid was found to be 0·963 gram-molecule of sodium pyrophosphate. At this point the liquid contains

$$Na_2SO_4 + \tfrac{1}{2}(H_4P_2O_7) + \cdot463(Na_4P_2O_7)$$
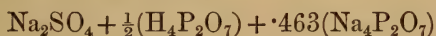
in equilibrium. The number ·463 therefore represents the comparative affinity of pyrophosphoric acid, except that as the acid is quadribasic the number found must be multiplied by 2 in order to bring it into comparison with bibasic acids. Therefore the index of pyrophosphoric acid is ·926. This acid being quadribasic, half a molecule contains the quantity of sodium requisite to saturate a molecule of sulphuric acid, and therefore only half a molecule of pyrophosphoric acid is set free.

In other words : It is found by experiment that the quantity of sodium pyrophosphate necessary to extinguish the reaction for free sulphuric acid with one thousand molecules of that acid, is 963 molecules ; out of this, five hundred molecules of pyrophosphoric acid are set free as just mentioned, and there remain 463 molecules of undecomposed pyrophosphate. This number 463 multiplied by 2 because of the basicity of the acid, and divided by 1000 to make it correspond to one molecule of sulphuric acid, gives ·926 as the index of pyrophosphoric acid.

The state of equilibrium is always conditioned by the degree of concentration. If to any solution of sulphuric acid a salt is added in just sufficient quantity to extinguish the sulphuric-acid reaction, it is then only necessary to add a little water and the equilibrium is at once changed ; a certain portion of the salt that had been added is re-formed and the sulphuric reaction reappears. In order, therefore, to obtain true comparative results, it is necessary to use the sulphuric acid always at exactly the same dilution and to add the dry salt to it.

The affinity of sulphuric acid for water is a most important factor in all determinations of this nature. Mendeléef indeed expresses the opinion [*] that most of the affinities hitherto

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[*] 'Principles of Chemistry,' English edition, vol. i. p. 377, footnote.

determined are unreliable for want of sufficient exactitude in this respect.

To show how much precaution is needed the following reactions may be mentioned.

When 4 cub. centim. of normal sulphuric acid are added to 40 cub. centim. of normal solution of sodium nitrate, not a trace of free sulphuric acid can be detected in the liquid. In consequence of the large excess of sodium salt the sulphuric acid has been completely taken up by the sodium, with of course an expulsion of an equivalent quantity of nitric acid.

But when, instead of 4 cub. centim. of normal sulphuric acid we use 40 cub. centim. of decinormal acid, then, although the quantities of acid and of salt are exactly the same, the equilibrium is completely changed. The greater quantity of water present by reason of its affinity for sulphuric acid counteracts to some extent the affinity of the sodium. Free sulphuric acid exists in the solution, and is abundantly indicated by the herapathite test.

This difference may be even more strikingly shown in the following manner :—Taking the mixture of 4 cub. centim. of normal sulphuric acid and 40 cub. centim. of normal solution of sodium nitrate, let a drop be placed in each of two small porcelain basins previously slightly warmed. To one of them let a single drop of distilled water be added, and then the herapathite test to both. In a few minutes the one which has received the drop of water will show well-marked crystallizations of herapathite, whilst the other will not show a trace. The effect of dilution in changing the equilibrium of the solution of a base with mixed acids is thus made visible to the eye by a chemical reaction. Hitherto it has been a deduction from physical changes requiring great delicacy of measurement. Results of a precisely similar character were obtained when potassium bromide was substituted for sodium nitrate, and are no doubt of general occurrence.

The applicability of this method proved to be a good deal restricted owing to the tendency of many acids when set free to decompose the herapathite reagent. For this reason the affinities of hydrobromic, hydriodic, chloric, iodic, and nitric acids could not be measured with accuracy, although many attempts, sometimes as many as 30 or 40 or more, were made to get reliable results. This work, however, was not entirely thrown away. It demonstrated that *chloric acid* has the strongest affinity for bases of any known acid. It might have been expected *à priori* that a highly oxidized acid of chlorine would have stronger affinities than chlorine hydride.

It also showed that the comparative affinity of nitric acid has hitherto been placed somewhat too high. Taking hydrochloric acid as 100, nitric acid scarcely exceeds 75.

The weaker acids, being for the most part without action on the test solution, give satisfactory results. Oxalic and tartaric acids must, however, be excepted, the acid set free tends to form acid salts of sparing solubility, these are precipitated: thus the conditions are changed.

The results obtained are here tabulated :—

Hydrochloric acid	29·37	13·68	100
Succinic....................	1·21	0·21	1·54
Acetic	2·28	0·14	1·02
Citric.................. ...	1·02	0·53	3·87
Pyrophosphoric	0·963	0·926	6·77
Tungstic	1·2	0·2	1·46

The first column of this table shows the absolute number of molecules of the sodium salt which must be added without regard to the basicity of its acid, in order that one molecule of sulphuric acid may be so completely saturated with base as no longer to give a reaction for free sulphuric acid.

In the second column these numbers are modified in such manner as to cause them to justly represent the comparative affinity of the acid. With monobasic acids the number of molecules is divided by 2, with quadribasic acids it is multiplied by 2. For a tribasic acid it is multiplied by $\frac{3}{2}$. Bibasic acids only remain unchanged. Next, unity is subtracted because it is always the excess of the salt which must be present in order to keep the sulphuric acid saturated with base that gives the measure of the affinity of the acid. Were this correction not applied, the entire result would be vitiated.

The third column gives the numbers as they appear when hydrochloric acid is taken as 100.

Instead of adding salts of different acids to sulphuric acid, we may add various acids to a salt formed by the union of sulphuric acid to a strong base, for example, to sodium sulphate.

Sulphuric acid is now recognized as being a weaker acid than hydrochloric, and yet we have seen that it is able to detach a certain quantity of base from a chloride. Further,

that if the chloride is present in sufficient excess, the sulphuric acid may take up enough base to completely saturate itself. The general fact that a certain quantity of acid may be expelled from a salt by another acid, even much weaker than the first, has been shown by the researches of Thomsen and of Ostwald. So that if, for example, we add acetic acid to a solution of sodium sulphate, a distinctly recognizable quantity of sulphate is decomposed and converted into acetate. A condition of equilibrium is produced in which the liquid contains both acids in a free state and both salts. In some way that we do not yet understand the presence of the free acid maintains the combined acid in its combination. The sodium acetate exists only by virtue of the free acetic acid present.

The existence of this state of equilibrium was first proved by Thomsen, who deduced it from the thermochemical changes which took place on mixing the solutions. Ostwald reached similar conclusions by making accurate determinations of the changes of volume and, consequently, of specific gravity which resulted from the mixing of the solutions, and in other ways.

In both these cases the conclusions are reached by logical deductions from the phenomena observed. But with the aid of the herapathite test, the expulsion of sulphuric acid by a very much weaker acid can be rendered immediately evident to the eye. Thus if to the solution of sodium sulphate we add acetic acid, and place two or three drops of the mixture in a warm porcelain basin and add some of the test liquid to it, in a few minutes we have a great number of small black rosettes of herapathite which crystallize out. Solution of sodium sulphate not containing acetic acid gives no such reaction with the herapathite test. It dries up to a pale yellow residue.

Acids vary very much in their ability to detach sulphuric acid from soda. The following acids, when added to sodium sulphate and tested by the herapathite test, give the results here noted.

Malic acid, gives an abundant crystallization.
Succinic acid, acts similarly.
Lactic acid, a moderate reaction.
Mucic acid, about the same as lactic.
Vanadic acid, traces.
Arsenic acid, abundant crystallization.
Hippuric acid, distinct traces.
Salicylic acid, distinct crystallization.

Of course the stronger organic acids, tartaric, oxalic, and citric, separate sulphuric acid with abundant crystallizations of herapathite when they are made to act on sodium sulphate

and the test is applied. It was observed that an acid oxalate acts like a free acid. Thus, when a solution of potassium binoxalate or quadroxalate is added to one of sodium sulphate, sulphuric acid is detached precisely as if free oxalic acid had been used.

It is clear that extremely weak acids, such as hippuric and salicylic, are able to take a certain quantity of base even from so strong an acid as sulphuric, setting free a recognizable quantity of this latter acid. Carbonic acid is still weaker than these. Ostwald, in determining the relative affinities of acids by the rate of the decomposition of acetamide and by the inversion of cane-sugar, found no appreciable effect from carbonic acid. It therefore became of interest to ascertain if any sensible decomposition of sodium sulphate would result from the action of this acid.

Perfectly pure carbonic anhydride was passed for a long time through a solution of sodium sulphate without setting free a recognizable trace of sulphuric acid. This was expected, the experiment was only preliminary to its repetition under pressure.

For this purpose sodium sulphate with the test solution was placed in one leg of a bent tube, in the other leg was placed sodium bicarbonate; and the tube was sealed. Heat was gradually applied to the bicarbonate. In the second trial the pressure was raised so high that the stout glass tube was ultimately shattered with violence. The leg containing the test liquid and sulphate had been secured in a clamp and remained uninjured. The liquid therefore had been subjected to the action of carbonic anhydride at a high pressure—it, however, gave no indications of a separation of traces of sulphuric acid under its action. It is to be remarked that this test is more decisive than if a solution of sodium sulphate had been used and had been tested afterwards. For in this last case, on release of the pressure, the reaction might readily be reversed with recombination of sulphuric acid, had any been liberated. But with the test liquid present during the pressure this reversal could not take place.

Carbonic anhydride, therefore, does not even under pressure set free any portion of sulphuric acid from sodic sulphate.

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The reactions described in this paper indicate :—

1. That when to free sulphuric acid a salt is added in sufficient quantity to cause the whole of the sulphuric acid to saturate itself with the salt-base, it is possible by means of the herapathite test to determine the exact point of such

saturation. At this point there will necessarily be as much of the acid at first combined with the base, now free in the solution, as corresponds to one molecule of a bibasic acid, that is two of a monobasic acid, half a molecule of a quadribasic acid, &c. From this we can deduce the exact nature of the resulting equilibrium.

2. That a series of equilibria thus obtained with different salts enables us to determine the comparative strength of the affinities of the acids of those salts.

3. That the fact, already proved in other ways, that even small quantities of weak acids, added to sulphates, will set free a certain quantity of sulphuric acid can, by means here given, be for the first time rendered visible to the eye by a well-marked chemical reaction.

LVI. *On the Design and Winding of Alternate-Current Electromagnets. By* Silvanus P. Thompson, *D.Sc., F.R.S., and* Miles Walker[*].

1. IN designing electromagnets for use with alternate currents various considerations enter which do not enter into the design of electromagnets for use with continuous currents. Chief of these considerations are the self-inductive action of the windings, and the frequency of the alternation of the current.

As with continuous-current electromagnets, so with alternate-current magnets, the degree to which magnetization is carried in the magnetic circuit of given configuration depends upon the number of ampere-turns of the excitation. The methods of predetermining the number needed to produce any desired degree of magnetization are too well known to need any reference. Our present aim is to show how to determine the winding which will, under given circumstances as to frequency, voltage, &c., produce any desired number of ampere-turns.

2. As a preliminary, however, it is needful to touch upon the point whether an electromagnet (properly laminated, it is understood) will give an equal pull, when excited with an equal number of ampere-turns of alternating current.

Since the pull of an electromagnet upon its armature depends upon the normal tension along the magnetic field integrated over the area of the pole-face, and this tension

is proportional to the square of the intensity of the magnetic flux, then, if this flux were proportional to the number of ampere-turns of excitation (as would be the case if the permeability were constant), the pull would be proportional to the square of the number of ampere-turns. Now the ampere-meters for alternate currents operate upon principles that cause them to indicate the square root of the mean square values of the current. Hence it follows that, if permeability were constant, the pull should be proportional to the square of the current, whether the current be continuous or alternating. But since, with an alternating current of the same nominal value as a continuous current, the magnetism is carried at each period to a point considerably higher than with the continuous current, and since also at the higher degrees of magnetization the permeability is lower, it follows that the pull of the electromagnet when excited by alternate currents ought to be slightly less if the excitation is so great as to carry the magnetization into the regions commonly spoken of as approaching saturation. The pull ought to be independent of the frequency of the alternation provided this exceeds a certain minimum.

Fig. 1.

Experiments made show that these views are justified in practice.

An electromagnet of the form shown in fig. 1 was made up of iron stampings about 0·5 millim. thick.
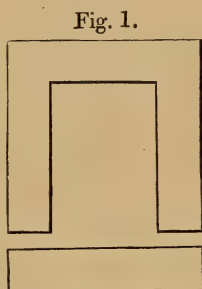
The principal dimensions were as follows :—

Mean length of limbs and yoke .	38	cms.
Breadth of limb	3·1	cms.
Gross thickness of limb . . .	2·54	cms.
Nett thickness of limb	2·1	cms.
Nett cross section of limb . . .	6·5	sq. cms.
Width between limbs	6·3	cms.
Total length of armature . . .	12·7	cms.

The stampings of the armature were of the same thickness, number, and breadth as those of the electromagnet. In the succeeding experiments the electromagnet was wound with 163 turns of copper wire 2·03 millim. in diameter, and the armature was separated from the pole-faces by a distance-piece of wood 0·952 centim. thick.

TABLE showing Pull and Different Frequencies with various Currents.

Exciting Current. Amperes.	Mean lines per sq. centimetre.	Pull, in grammes, with Continuous Current.	Pull, in grammes, with Alternate Current.
A. *At a frequency of* 30 *periods per second.*			
8	2300	280	280
12·5	3600	820	820
B. *At a frequency of* 60 *periods per second.*			
8	2300	280	280
10·2	2900	530	550
C. *At a frequency of* 90 *periods per second.*			
4	800	60	60
4·2	1100	100	100
10·2	2900	530	530
21	5600	2400	2200
D. *At a frequency of* 120 *periods per second.*			
13·2	3900	900	900
21	5600	2400	2200

These experiments show that the pull was exactly the same when the intensity of the flux did not exceed 4000 lines per square centimetre. At higher degrees of magnetization the pull with alternate currents is slightly less.

It may be remarked that at higher intensities and with higher frequencies, eddy-currents, if any are present, will produce, for an equal flow of exciting current, a greater demagnetizing action, and therefore lessen the pull. On the other hand, if the current is supplied at a constant (alternating) voltage, eddy currents do not decrease the magnetization but cause more current to flow in proportion.

Another experiment was made with a solenoidal electro-magnet with a laminated U-form plunger belonging to a

Brush alternate-current arc-lamp. This plunger with attached mechanism weighed about 820 grammes, and was arranged to be drawn up into position by a current of 10 amperes. This plunger was loaded with various weights and the current required to raise it was measured, with the following results :—

Total weight.	Continuous Current. Amperes.	Alternate Current. Virtual Amperes.
820	10	10
933	17·2	18
1039	18·2	19·5
1276	25	26·5
1601	31	33
1728	36	40

3. When alternate currents are supplied at a given voltage to an electromagnet having a given configuration of the magnetic circuit, and it is desired to produce by a winding any given number of ampere-turns of excitation, it is obvious that there are many ways of attaining the result with coils of various sizes and numbers of turns. If the resistance of the coil is so small relatively to the inductance as to be negligible, then there will only be one possible solution as to the number of turns. If, however, the resistance of the coil is of a magnitude comparable with that of its inductance, then there are various possible solutions, for an equal number of ampere-turns may be produced by using currents of different strengths and coils of different numbers of turns. In the cases of different windings the lag of phase of the currents will be different. If the resistance is large relatively to the inductance, the difference of phase between the current and the impressed volts will be small, and the wasted watts large. If the inductance is large relatively to the resistance, the difference of phase will be nearly 90°; and the current will be nearly wattless, the efficiency being relatively high.

It is in accordance with good constructive practice to use such frequencies in the supply, and coils of such relatively high coefficients of self-induction as to justify the assumption, for the purpose of design, that the inductance is the important, and the resistance of the coil the unimportant matter. However, to bring the calculations to bear upon all cases that may occur, both resistance and inductance have been taken into consideration.

Let the impressed volts be called V, the current i (both being square-root of mean square values), the resistance of the coil R, its coefficient of self-induction L, the frequency of the period of alternation n, and the number of windings W. The inductance will then be $2\pi n$L, which for brevity may be written pL. Then the impedance will be $\sqrt{R^2 + p^2L^2}$. The relation between volts and amperes in the coil will be expressed as

$$V = i\sqrt{R^2 + p^2L^2}.$$

The angle of lag being called ϕ, its sine will have the value

$$pL \div \sqrt{R^2 + p^2L^2}.$$

Hence we have the following relation :—

$$V . \sin \phi = ip\text{L} ; \quad . \quad . \quad . \quad . \quad . \quad (1)$$

these being equivalent expressions for the effective part of the volts that is employed to balance the counter-electromotive force of self-induction in the coils. Now L is proportional to the square of the number of windings ; and may be written $= k\text{W}^2$, where k is the coefficient of self-induction of a single turn, and W the number of windings.

Now, let the prescribed number of ampere-turns that are to be produced be called $Z = i$W. Inserting these values in (1) we obtain the expression

$$V \sin \phi = kp\text{WZ} ; . \quad . \quad . \quad . \quad . \quad (2)$$

and finally

$$W = \frac{V \sin \phi}{kp\text{Z}} ; \quad . \quad . \quad . \quad . \quad . \quad (3)$$

which is the relation sought.

4. The quantity k denoted above, the coefficient of self-induction of a single turn, depends upon the dimensions of the iron parts of the magnetic circuit and upon those of the air-gap, as well as upon the permeability of the iron. If the magnetization is not carried beyond 5000 lines per square centimetre, the permeability may be considered as constant. But k will decrease with any increase in the reluctance of the magnetic circuit, such as the lengthening of the air-gap. On the contrary, as the armature is attracted up toward the poles k increases. The quantity k represents the number of magnetic lines ($\times 10^{-9}$) which permeate the magnetic circuit when one ampere circulates in a single turn of wire around the core. We have only to multiply k by the square of the number of windings to obtain the coefficient of self-induction of any coil subsequently to be wound upon this magnetic circuit. The quantity k must itself be experimentally

determined. This can be done by winding upon the magnetic circuit an experimental coil having a known number of turns w, and a known resistance r. Using this coil, measure the virtual current c which passes when it is supplied at a voltage v of frequency n. During the experiment the armature should be fixed, say by wooden distance-pieces, in the position which it will occupy in use. Then the coefficient of self-induction l of the temporary coil will be

$$l = \sqrt{v^2 - c^2 r^2} \div \sqrt{4\pi^2 n^2 c^2}.$$

Then l being thus experimentally determined, it follows that $k = l/w^2$.

From the equation (3) we see that V, p, and k being constant, there is a certain maximum number of windings which must not be exceeded if we are to get the prescribed number of ampere-turns of excitation; for $\sin\phi$ cannot be greater than unity. If this maximum number of windings is exceeded, the result will be to give fewer ampere-turns. This is easily seen if equation (3) be put into the form,

$$Z = \frac{V \sin\phi}{kp\,W}. \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (4)$$

Other things being equal, *the ampere-turns are inversely proportional to the number of windings.* This, at first sight, seems an anomaly; but it is easily understood when we remember that the self-induction, and therefore the lessening of the current, is proportional to the square of the number of turns; so that whilst we are increasing our turns we are reducing our amperes in a much greater ratio.

Having ascertained k, the only other factor to be determined is $\sin\phi$. This in most practical cases can be assumed to be unity, since with the usual frequencies of supply and using magnets with iron cores, there is no difficulty in keeping the resistance negligibly small even when the number of windings is at the required maximum, so that ϕ is very nearly $90°$. This will be seen from the results given below obtained from an actual magnet. In most ordinary cases, then, we merely write

$$W = V/kpZ; \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (5)$$

and, having calculated W, we find what current the wire will have to carry from the equation $i = ZW$. If there is room, and in most cases there will be ample, we may wind with thicker wire than is necessary to carry the current; but there is no advantage in using thicker wire than such as makes R practically negligible.

5. The following results are from actual experiment. The core and armature were those already described in relation to fig. 1. The iron core was wound with 140 turns of copper wire, 1·22 millim. in diameter, for the purpose of first determining k when the armature was at the distances of 9·52, 6·35, 3·17, and 0 millim., respectively, from the poles. The resistance of the wire when heated by carrying 12 amperes was 0·3 ohm, and the frequency 93 periods per second. The fourth and fifth columns are worked out from the formulæ given above ; for instance, in the first case

$$l = \frac{\sqrt{(31)^2 - (12 \times 0.3)^2}}{2\pi \times 93 \times 12} = 0.00434.$$

$$k = \frac{0.00434}{(140)^2} = 0.221 \times 10^{-6}.$$

Air-gap (millimetres).	Virtual Volts at terminals of coil.	Virtual Amperes.	Coefficient of Self-induction l.	Self-induction of one turn. k.
9·52	31	12	0·00434	0.221×10^{-6}
6·35	35·6	12	0·005	0.225×10^{-6}
3·17	46·8	12	0·00658	0.336×10^{-6}
0	51	2·76	0·033	1.68×10^{-6}

Suppose it were now required to wind the iron core so as to obtain 2400 ampere-turns when the armature was distant 9·52 millim. from the poles, using 50 volts and the same frequency as before.

Taking the equation (5) we obtain :

$$W = \frac{50}{0.221 \times 10^{-6} \times 2 \times 3.1416 \times 93 \times 2400} = 163 \text{ (approx.).}$$

Accordingly 163 turns of wire 2·03 millimetres in diameter were wound upon the core. The current found, under the above conditions, to flow through the coil was 14·9 amperes, as measured by a Siemens's electrodynamometer. This shows that the coil produced 2430 ampere-turns, the error being well within what may be expected when using commercial measuring-instruments.

Some other results obtained with this magnet are given below.

Coil 163 turns ; resistance (hot) 0·15 ohm.				
Air-gap (millimetres).	Virtual Volts.	Virtual Amperes.	Coefficient of self-induction.	Self-induction of one turn.
9·52	50	14·9	0·00574	$0·216 \times 10^{-6}$
6·35	50	12	0·00714	$0·268 \times 10^{-6}$

Coil 274 turns ; resistance (hot) 0·6 ohm.				
9·52	50	5	0·01712	$0·228 \times 10^{-6}$
6·35	50	4·4	0·0194	$0·259 \times 10^{-6}$
3·17	50	3·5	0·0244	$0·326 \times 10^{-6}$

6. An advantage of the alternate-current electromagnet is the greater constancy in the pull which it exerts over a given range. If supplied at constant voltage a fairly constant pull on the armature can be obtained over a considerable range. The reaction set up by the core tends to set up a back-electromotive force the limiting value of which is equal to the impressed voltage. If the resistance of the coil were actually zero and the magnetic leakage also negligible, this limiting value would be attained. Now suppose that when acting upon its armature at a distance the self-inductive reaction chokes the current down to a certain value, the magnetization of the core going round cycles between definite maxima. Suppose the core to be drawn in nearer to the pole, the reluctance of the magnetic circuit is lessened, and fewer ampere-turns will suffice to produce an equal magnetization ; but because the reluctance is lessened the coefficient of self-induction is correspondingly increased, and the current choked in corresponding proportion. These two effects counterbalance one another, the magnetization going round cycles of practically the same amplitude as before. Hence the pull will be practically unchanged, save in so far as any change in the magnetic leakage at the different positions of the armature comes in to affect the question by weakening the field between the pole-faces and the armature. Were the pole-faces made relatively large so as to obviate the tendency

to leakage and ensure the field being nearly uniform in the gap-spaces, the pull should be also very nearly constant throughout a range equal to at least one third of the breadth of the pole-face.

7. [*Added April* 10*th*, 1894.]—It is useful also to know the ratio between the different voltages that are needed, for a given electromagnet, to produce an equal number of ampere-turns with alternating and continuous electromotive forces.

Let V_a stand for the alternating volts and V_c for the continuous volts which must be applied to the terminals of the coil in order to produce equal virtual amperes. Then

$$\frac{V_a}{V_c} = \frac{\sqrt{R^2 + p^2 L^2}}{R}. \quad . \quad . \quad . \quad . \quad (6)$$

When, as is generally the case, R is small compared with pL, we may take as a sufficient approximation

$$\frac{V_a}{V_c} = \frac{pL}{R}. \quad . \quad . \quad . \quad . \quad . \quad (7)$$

The alternate voltage ratio is proportional to the frequency and to the time-constant of the electromagnet.—For this ratio we may, on certain assumptions, find an expression in terms of the dimensions of the core and coil. Confining ourselves to the case where the magnetic circuit is closed we may find the value of L as follows :—

Let l_1 be the length (in centimetres) of the iron magnetic circuit, A_1 its cross section, v_1 its volume, m_1 its mass in grammes, μ its permeability, and S the number of windings in the coil. Now $m_1 = 7 \cdot 79 v_1$. Then L (in henries) will be

$$L = 4\pi A_1 \mu S^2 / 10^9 l_1 = 4\pi v_1 \mu S^2 / 10^9 l_1{}^2 = 4\pi m_1 \mu S^2 / 7 \cdot 79 \times 10^9 l_1{}^2.$$

Assuming that B does not exceed 6000 lines per square centimetre, we may take for ordinary wrought-iron sheet $\mu = 2000$, and inserting this we obtain

$$L = S^2 m_1 / 310,000 \, l_1{}^2.$$

Further, let l_2 be the mean length of one turn of the copper winding, A_2 the cross section of the copper wire, k its conductivity (mhos per centimetre cube $= 10^6 \div 1 \cdot 63$), v_2 the volume of copper $(= SA_2 l_2)$, and m_2 the mass of copper $(= 8 \cdot 8 v_2)$. Then we have for the resistance of the coil

$$R = l_2 S / A_2 k = l_2{}^2 S_2{}^2 / v_2 k = 8 \cdot 8 l_2{}^2 S_2{}^2 / m_2 k.$$

Inserting these values for L and S we obtain :—

$$\frac{V_a}{V_c} = \frac{pL}{R} = \frac{2\pi n S^2 m_1}{310000 l_1{}^2} \times \frac{m_2 . 10^6}{8 \cdot 8 l_2{}^2 S^2}.$$

$$\frac{V_a}{V_c} = 1 \cdot 41 n \frac{m_1 m_2}{l_1{}^2 l_2{}^2} \quad . \quad . \quad . \quad . \quad . \quad (8)$$

It is, however, doubtful, since the magnetic circuit contains two joints, whether so high a value as 2000 can be expected in ordinary work for μ. In that case the coefficient 1·41 will be lower. With the electromagnet described above, at a frequency $n = 93$, and with the armature in contact, the coefficient was 0·6 instead of 1·41. This is tantamount to saying that the working permeability was only 850. As so arranged, L being 0·044, the inductance pL was 25·26 ohms, and R was 0·15 ohm. The alternate voltage ratio was therefore about 170.

As the armature was removed from proximity to the poles the self-induction, and therefore the impedance, fell, making the voltage ratio for equal currents lower. When the armature was at 3·17 millim. the voltage ratio fell to 34, and at 9·52 millim. to 21·5.

It was stated above that in ordinary cases the ratio pL/R might be taken instead of the more complete expression of equation (6). If it is desired to obtain a nearer approximation to $\sqrt{R^2 + p^2 L^2}/R$ than is afforded by simply neglecting the R under the square-root sign, we may take the value

$$\frac{V_a}{V_c} = \frac{p\text{L}}{\text{R}} + \frac{\text{R}}{2p\text{L}},$$

which, by reference to the preceding numerical instances, shows that the correcting term is really negligible, being in the first case, where pL/R was 170, only $\frac{1}{340}$, and in the last case, where pL/R was 21·5, only $\frac{1}{43}$, less than $\frac{1}{8}$ of 1 per cent.

8. [*Added April 27th.*]—Lastly, a very simple expression can be found for the number of windings, in terms of any desired mean value of the magnetic flux **N** in the iron. For if the iron of cross-section A is subjected to cycles of magnetization in which the mean value of the permeation is **B**, the mean flux is **N** = A**B**, and if the frequency be n periods per second, the self-induced electromotive force in W windings surrounding the iron will be equal to $2\pi n$W**N** ÷ 10^8 volts. If, then, the resistance is negligibly small, this may be equated to **V**, the mean volts of supply, whence we obtain at once

$$\text{W} = \frac{\text{V} \times 10^8}{p\textbf{N}}. \quad \ldots \ldots \quad (9)$$

For example :—Suppose that in the above magnet it were desired to obtain a permeation of 4000 lines to the square centimetre, the total number of lines **N** would equal the area A (6·5 square centim.) multiplied by 4000, or **N** = 26,000. Taking the volts as 50, and the periods per second as 93, we find by formula (9), W = 329.

LVII. *The Second Law of Thermodynamics.*
By S. H. Burbury, *F.R.S.*[*]

IN a statistical system of molecules let T be the mean kinetic energy, and $v_1 \ldots v_r$ certain " controllable " co-ordinates, according to the notation used by Messrs. Larmor and Bryan in their Report on Thermodynamics. Let ∂Q be the energy that must be supplied, or spent in external work, when T becomes $T + \partial T$, and v_1 becomes $v_1 + \partial v_1$, &c. The object of this paper is to find the most general condition that will make $\dfrac{\partial Q}{T}$ a complete differential of a function of T, $v_1 \ldots v_r$. It will be found to be the same condition which is necessary to make the motion stationary with T, $v_1 \ldots v_r$ constant.

1. Let the state and position of a molecule be defined by the n generalized coordinates $x_1 \ldots x_n$ with corresponding velocities, and the r controllable coordinates $v_1 \ldots v_r$. It is assumed that the v's vary so slowly that their velocities may be neglected, but their components of momentum shall be $V_1 \ldots V_r$. Let U be the potential, τ the kinetic energy of a molecule, $E = U + \tau$.

2. Let us assume provisionally that if the molecule be started from any position with any velocities, $v_1 \ldots v_r$ being maintained constant, its motion will be periodic ; and therefore on average of time $\dfrac{dV}{dt} = 0$ for each v.

3. Generally, if only the conservative forces act, $v_1 \ldots v_r$ will vary. We must then apply external constraining forces $P_1 \ldots P_r$ to prevent $v_1 \ldots v_r$ from increasing.

By Lagrange's equations,

$$\frac{dV}{dt} = \frac{d\tau}{dv} - \frac{dU}{dv} - P \text{ for each } v;$$

and since $\dfrac{dV}{dt} = 0$ on average of time,

$$P = \frac{d\tau}{dv} - \frac{dU}{dv} \text{ on average of time.}$$

4. For any given constant values of $v_1 \ldots v_r$ we may have many different motions of the molecule, all of this character, but with different values of $\bar{\tau}$, the mean kinetic energy. So with the same $\bar{\tau}$ we may have different values of $v_1 \ldots v_r$. If we wish to make the system pass from an original motion, in

which these quantities are $\bar{\tau}$, $v_1 \ldots v_r$, to a varied motion, in which they are $\bar{\tau} + \partial \bar{\tau}$, $v_1 + \partial v_1$, &c., we have (1) to supply energy ∂E, (2) to do work $\Sigma P \partial v$ against the constraining forces. The whole energy required is $\partial E + \Sigma P \partial v$, or

$$\partial \bar{\tau} + \partial \overline{U} + \Sigma \left(\frac{d\tau}{dv} - \frac{dU}{dv} \right) \partial v.$$

5. Now let there be a great number, N, of such molecules, all with the same values of $v_1 \ldots v_r$, but different values of $\bar{\tau}$ and E. According to the provisional assumption above made, the N molecules are describing periodic motions with different periods, and with an infinite variety of phases. Owing to this variety of phases $\frac{dV}{dt} = 0$ for each V, not only on average of the time, but on average at any instant of all the molecules describing a given orbit. And if the whole motion be stationary, this property may hold even though the motions of individual molecules be not strictly periodic. We may then replace the provisional assumption, that each molecule is in periodic motion, by the assumption that $\frac{dV}{dt} = 0$ for each v.

6. Let $Nf(x_1 \ldots x_n)dx_1 \ldots dx_n$, or, shortly, $Nfd\sigma$, be the number of molecules whose coordinates at any instant lie between the limits

$$\left. \begin{array}{c} x_1 \text{ and } x_1 + dx_1, \\ x_2 \text{ and } x_2 + dx_2, \\ \text{\&c.} \end{array} \right\} \quad \ldots \quad \ldots \quad (A)$$

Then $fd\sigma$ is the chance that any given molecule at any instant shall belong to that class.

Similarly let $f'(\dot{x}_1 \ldots \dot{x}_n)d\dot{x}_1 \ldots d\dot{x}_n$, or, shortly, $f'd\sigma'$, be the chance that for a given molecule at any instant the velocities shall lie between the limits

$$\left. \begin{array}{c} \dot{x}_1 \text{ and } \dot{x}_1 + d\dot{x}_1, \\ \dot{x}_2 \text{ and } \dot{x}_2 + d\dot{x}_2, \\ \text{\&c.} \end{array} \right\} \quad \ldots \quad \ldots \quad (B)$$

Whether or not f' be a function of the coordinates $x_1 \ldots x_n$, we must have

$$\int f'd\sigma' = 1.$$

The chance that a given molecule shall at any instant belong to both class A and class B is $ff'\,d\sigma\,d\sigma'$, or, as we will write it, $F\,d\sigma\,d\sigma'$.

2 R 2

7. With this notation, if the bar now denotes mean values for the whole system,

$$\overline{U} = \iint U\,F\,d\sigma\,d\sigma' = \int U f\,d\sigma \int f'\,d\sigma'$$

$$= \int U f\,d\sigma.$$

Similarly,

$$\overline{\frac{dU}{dv}} = \iint \frac{dU}{dv}\,F\,d\sigma\,d\sigma'$$

$$= \int \frac{dU}{dv} f\,d\sigma.$$

Also

$$\overline{\frac{d\tau}{dv}} = \iint \frac{d\tau}{dv}\,F\,d\sigma\,d\sigma'.$$

And if we denote by T the mean kinetic energy of a molecule for the whole system,

$$T = \iint \tau\,F\,d\sigma\,d\sigma'.$$

8. We may now suppose $v_1 \ldots v_r$ to vary in any manner for all the molecules simultaneously. Further we may, with or without variation of $v_1 \ldots v_r$, make T vary. Now τ is a quadratic function of $\dot{x}_1 \ldots \dot{x}_n$, with coefficients which may be functions of $v_1 \ldots v_r$ as well as of $x_1 \ldots x_n$. And therefore when $v_1 \ldots v_r$ vary, T, or $\iint \tau\,F\,d\sigma\,d\sigma'$, will generally vary. But if $v_1 \ldots v_r$ be constant, T can only vary by the variation of F. We might suppose F a function of a variable θ not contained in τ or U. Then with $v_1 \ldots v_r$ constant,

$$\partial T = \partial\theta \iint \tau \frac{dF}{d\theta}\,d\sigma\,d\sigma'.$$

And when $v_1 \ldots v_r$ also vary, the whole variation of T is

$$\partial T = \iint \Sigma \frac{d\tau}{dv}\partial v\,F\,d\sigma\,d\sigma' + \iint \tau \Sigma \frac{dF}{dv}\partial v\,d\sigma\,d\sigma'$$
$$+ \iint \tau \frac{dF}{d\theta}\partial\theta\,d\sigma\,d\sigma',$$

$$= \Sigma \overline{\frac{d\tau}{dv}}\partial v + \iint \tau\partial F\,d\sigma\,d\sigma',$$

or

$$\Sigma \overline{\frac{d\tau}{dv}}\partial v = \partial T - \iint \tau\partial F\,d\sigma\,d\sigma'. \quad . \quad . \quad . \quad (I.)$$

9. Again, since $\overline{U} = \iint U F \, d\sigma \, d\sigma'$,

$$\partial \overline{U} = \iint U \, \partial F \, d\sigma \, d\sigma' + \iint F \, \partial U \, d\sigma \, d\sigma',$$

$$= \iint U \, \partial F \, d\sigma \, d\sigma' + \iint F \Sigma \frac{dU}{dv} \partial v \, d\sigma \, d\sigma',$$

$$= \iint U \partial F \, d\sigma \, d\sigma' + \Sigma \overline{\frac{dU}{dv}} \partial v.$$

Therefore

$$\partial \overline{U} - \Sigma \overline{\frac{dU}{dv}} \partial v = \iint U \partial F \, d\sigma \, d\sigma'. \quad . \quad . \quad . \quad \text{(II.)}$$

In the same way, since $\overline{U} = \int U f \, d\sigma$, we find

$$\partial \overline{U} - \Sigma \overline{\frac{dU}{dv}} \partial v = \int U \partial f \, d\sigma. \quad . \quad . \quad . \quad \text{(II.}a\text{)}$$

10. If ∂Q be the energy imparted to the system or spent in work when the variation takes place,

$$\partial Q = \partial T + \partial \overline{U} + \Sigma P \partial v$$

$$= \partial T + \partial \overline{U} - \Sigma \overline{\frac{dU}{dv}} \partial v + \Sigma \overline{\frac{d\tau}{dv}} \partial v, \text{ because } \frac{dV}{dt} = 0,$$

$$= 2 \partial T + \iint U \partial F \, d\sigma \, d\sigma' - \iint \tau \partial F \, d\sigma \, d\sigma'$$

by (I.) and (II.). Therefore

$$\frac{\partial Q}{T} = 2 \partial \log T + \iint \frac{U}{T} \partial F \, d\sigma \, d\sigma' - \iint \frac{\tau}{T} \partial F \, d\sigma \, d\sigma'. \quad . \quad \text{(III.)}$$

11. We might now make $\dfrac{\partial Q}{T}$ a complete differential by assuming $F = \phi\left(\dfrac{\tau - U}{T}\right)$, where ϕ is an arbitrary function. But this solution must be rejected, because it will not make F vanish for all infinite values of τ and U.

12. But using (II.a) instead of (II.) we obtain instead of (III.)

$$\frac{\partial Q}{T} = 2 \partial \log T + 2 \int \frac{U}{T} \partial f \, d\sigma - \iint \frac{\tau + U}{T} \partial F \, d\sigma \, d\sigma'. \quad . \quad \text{(IV.)}$$

And now we obtain a solution in the form

$$F = \phi\left(\frac{\tau + U}{T}\right),$$

$$f = \psi\left(\frac{U}{T}\right),$$

where ϕ and ψ denote any functions. And since F and f must vanish for all infinite values of the variables, we are led to

$$F = C\epsilon^{-\lambda\frac{U+\tau}{T}},$$

$$f = C'\epsilon^{-\lambda\frac{U}{T}},$$

where λ is some positive numerical quantity, and C, C' are found from the conditions

$$C\iint F\, d\sigma\, d\sigma' = 1,$$

$$C'\int f\, d\sigma \quad = 1.$$

13. But these are the same conditions which make the motion stationary with $T, v_1 \ldots v_r$ constant. This has been satisfactorily proved for the case where the mutual action between the molecules is restricted to " binary encounters." (Watson's Kinetic Theory of Gases, second edition, p. 36.)

In the January number of this Magazine I have endeavoured to show that the same form of F gives stationary motion if we remove this restriction on mutual action.

14. If the necessity for making $\dfrac{\partial Q}{T}$ a complete differential can be established as a substantive law by independent evidence, the above investigation affords an independent proof of the distribution

$$C\epsilon^{-\lambda\frac{U+\tau}{T}}$$

for such a system as above described, and that whether the mutual action is restricted to binary encounters or not.

15. I have assumed that the continued products of differentials $d\sigma$ and $d\sigma'$ do not vary. If they do vary, that is in effect if the limits of integration vary, the assumption $F = \phi\left(\dfrac{U+\tau}{T}\right)$ will still make $\dfrac{\partial Q}{T}$ a complete differential.

LVIII. *Notices respecting New Books.*

Man; the Primeval Savage: his Haunts and Relics, from the Hill-tops of Bedfordshire to Blackwall. By WORTHINGTON G. SMITH, &c. Pages i–xvi and 1–349, with 242 Illustrations by the Author. 8vo. Stanford: London, 1894.

THE author of this interesting book makes a praiseworthy attempt to popularize the subject of Early Man, from a strictly scientific point of view, with the evidences of his existence, his modes of life, and his surroundings, in this part of the world at least. Mr. W. G. Smith has done much in judiciously searching for, and happily finding, tangible proofs of Man having occupied certain sites now buried beneath various deposits that have been left by lakes and rivers during repeated superficial changes of the land. Here some geological knowledge aids him; and, as an archæologist with a good eye for the recognition of differences between relatively old and new implements of flint, and of the chips and blocks left in places during their manufacture, he tries to piece together the broken history of Early Man once occupying parts of Bedfordshire, Hertfordshire, Middlesex, and Essex.

Freely using the results of similar observations made by others at various places, and recognizing the value set by anatomists on certain human bones as indicative of special races,—and by palæontologists on the particular characters of the more frequent bones of the lower animals found in gravels and other deposits of Quaternary age, Mr. Smith has thus added greatly to his former contributions to the Anthropological and other Societies.

In the first two Chapters he briefly treats of Primeval Man as known by his implements of stone, found in caves, gravels, and elsewhere, and by the rarely associated fragments of human skulls and skeletons, the more frequent bones of animals, and remains of plants; and by the comparison of the bones of some of the lowest races of mankind with those of the anthropoid apes. The probable ways and habits of the early savages, and their surroundings, are presented in picturesque descriptions by the pen and pencil of modern civilization forced to acknowledge the barbarous and disgusting habits of our probably cannibal progenitors. " Man at that time was not a *degraded* animal, for he had never been higher; he was therefore an exalted animal; and, low as we esteem him now, he yet represented the highest stage of development of the animal kingdom of his time " (page 59).

Of the primeval folk of England we have set before us by the artistic author four pictures. One of them (on the cover) is a woman sitting on a dead and broken tree-trunk, with her hair turned up in Egyptian style, and in " full dress," consisting of a waist-strap supporting a stone *hache*; and a club lies handy. The face of this savage is almost manly, perhaps tatooed at the corners of the mouth, if not moustached; and the ear is strongly pointed; a feature which still survives at Dunstable, according to page 51

and its woodcut. On the title-page a man and his two wives, with an infant-girl, make a fallen tree their resting-place by the water-side. They are destitute of even skins for raiment, and have no apparent belongings except a club near one woman, and a stone-weapon strapped to the waist of the other. Their luxuriant hair, carefully parted or otherwise arranged, barely hides their sharp-pointed ears; tatoo-marks seem to add width to the female mouths, whilst the man has a moustache. They are all looking earnestly in one direction (towards us, as if to be photographed), waiting for something or somebody.

The chief interest of the book is connected with the district round about Caddington, a village 30 miles north of London, 3 miles south-east of Dunstable, and 2 miles south-west of Luton. Here Mr. W. G. Smith has discovered very many man-made weapons and tools of flint, of very great antiquity, on the highest hill-tops of the Chalk, which are capped with stony clays, gravels, and brickearths. These deposits are described briefly at page 70, and in more detail, with carefully drawn sections, in subsequent pages. Flint implements occur in the upper clays and gravels, which are much distorted, and here and there pushed down, as it were, in violent curvatures, into the underlying brickearth. The last-mentioned deposit is about 50 feet thick in some places; and Mr. Smith found in it, at some 10 or 12 feet from the surface of the ground, one or more levels distinguished by small heaps of flints, artificially accumulated in some olden time; and he observed that, both among them and on the intervening spaces, many of the flints had been broken and "dressed," or shaped for use. He succeeded in fitting together hundreds of the flakes and pieces that had been disregarded and thrown aside by the primeval artificers of stone tools and weapons.

Carefully following out the indications of this tool-making area, Mr. Smith traces it, by sections, through Caddington Hill (page 64), as having been a part of an old land-surface, bearing one or more lakes or pools along a marshy valley; and on the valley-sides, near the water, the flint-folk must have lived and worked, leaving their refuse to mark what is termed a "palæolithic floor," because the tools have certain shapes, regarded as characteristic of the *older-stone-age* implements, or "palæoliths."

In the "upper red clay drift" of the brick-pits, smaller, more roughly shaped, ochreous or chocolate-coloured implements are met with; and these, evidently deposited long after the working-floor, or lake-side living-place, was covered up, were probably derived by the natural agency of water descending from neighbouring hills, and bringing with it the washings of some local ochreous capping, possibly very much older than any of the valley-deposits.

After describing these more or less stratified materials, and endeavouring to explain the conditions under which they were formed and modified,—and giving particulars of his long examination of the sections, and his persistent search for the actual pits

and strata in which the several forms were obtained,—the author attempts some observations about the fashions and the relative age of flint implements, but they have neither any special importance nor novelty.

The latter part of the book describes some of the relics of primeval man as found on the banks of the Lea, from its source near Dunstable, in Bedfordshire, to London; with a description of the already known primeval living-place or "palæolithic floor" at Stoke-Newington, London.

In Chapter XIII. we have traces of Primeval Man elsewhere, near the Lea, in South Beds and North Herts.

Chapters XIV. & XV. Traces of Primeval Man near the Lea in Middlesex and Essex, from Waltham to Tottenham, on the Border-Line of London; and from Tottenham to the Junction of the Lea with the Thames at Blackwall: with notes on Stone Weapons and Tools—the Most Ancient Implements; Implements of Medium Age; Implements of Least Palæolithic Age; Pieces of Implements Conjoined and Flakes Replaced; How Stone Implements were Made; worked Wood and Bone; Fossils as Beads; Fossil Bones; Shells of Land- and Freshwater Mollusca; Plant-Remains; Forgeries of Implements.

Chapter XVI. Mesolithic Implements.

Chapter XVII. Palæolithic Stones found by Neolithic Men and Reworked.

Chapter XVIII. Neolithic Implements and Keltic Relics, from South Bedfordshire to London:—Implements of Stone and Bronze; Earthworks, Roads, and Trackways near Dunstable; British Hut Foundations near Dunstable; Dene-Holes; Graves, Tumuli, Skeletons, Bones; Place-Names near Dunstable.

It is evident, and indeed partly stated, that Chapters XIII. to XVIII. consist of renewals and reprints of earlier notes and memoirs by the author and others, published in the Journ. Anthropological Institute, Proceed. Geologists' Association, Quart. Journ. Geological Society, 'Nature,' 'Natural Science,' Proceed. Essex Field-Club, 'Ancient Stone Implements of Great Britain,' 'Archæologia Cambrensis,' &c. In such a compilation, however, the references to papers by fellow-workers should be complete, and careful acknowledgement of all sources of information should be made in every case, so that the reader should distinguish what is not, from what is original, in the book before him.

The printing and paper are good. "All the Illustrations are original or taken from original sources." They have been admirably drawn (some after photographs) and reproduced on wood or otherwise, by the Artist-engraver, Mr. W. G. Smith, himself. The "archæological map of the Caddington and Dunstable district" clearly defines the topography of the author's discoveries; and another map shows a part of the north-eastern neighbourhood of London. The numerous illustrations comprise skulls, bones, stone tools and flakes, sections, local views, a few shells and fossils, and four neat and expressive ideal portraitures of the aborigines. We

are sorry that two of these clever pre-Raphaelistic pictures are not lodged in the text; one is on the title-page, and one indeed is seen only gilded on the cover.

Altogether, this interesting work, partly descriptive of a new set of discoveries, and partly a compilation of more or less relative matter, is calculated to incite a taste for seriously hunting up the history of Primeval Man; and, by showing how and where the study may be practically followed, it will satisfy, to some extent, many enquiring minds, putting them on the right lines for investigation, and affording some clues to other and more important systematic works on archaic anthropology.

LIX. *Intelligence and Miscellaneous Articles.*

ON THE MAGNETIZATION OF IRON AND NICKEL WIRE BY RAPID ELECTRICAL OSCILLATIONS. BY PROF. I. KLEMENČIČ.

BY the aid of the formulæ of Lord Rayleigh and Stefan the author endeavoured to determine the strength of magnetization, or, in other words, the value of μ, from the disengagement of heat which occurs in a magnetizable wire when electrical vibrations are passed through (number of vibrations about 9×10^7). The development of heat was measured by means of a delicate thermoelement near the wire under experiment, and was each time compared with the disengagement of heat in a non-magnetized wire. Observation gave the following values for μ:—soft iron, 118; steel (piano wire), soft 106, hard 115; Bessemer steel, soft 77, hard 74; nickel, 29. These values agree well with those which Baur and Lord Rayleigh found for very feeble magnetic forces. As the experiments of these observers teach, the permeability is a constant magnitude up to certain values of the magnetizing force while it thus rapidly increases. The present observations show that in these experiments μ varies within a certain range. This fact can be explained either by assuming that the magnetizing forces used here are very feeble, and of the order of magnitude of those strengths of field in which μ is really constant; or by assuming that we are dealing with much greater magnetizing forces, but that the magnetization cannot follow the rapid change so quickly as to reach that part of the curve of magnetization which corresponds to the variable and far greater values of μ. An approximate estimation of the field-strengths under consideration shows that at any rate on the surface of the wire and at the beginning of the oscillations we have magnetizing forces which are several hundred times as great as that limit within which μ is constant. There would accordingly in this case be a retardation of the magnetization, which, however, must not be confounded with hysteresis. It must in this be assumed that the results of Baur and of Lord Rayleigh which refer to longitudinal magnetization are also applicable to circular magnetization.

Within the limits of the constant μ there is no remanent magnetism; the magnetization in this region is similar to the deformation of a body within the limits of elasticity, while the further stages

of magnetization are to be compared with permanent deformations; an analogy which Maxwell had already pointed out. That part of the magnetization which can be applied technically is in the region corresponding to the permanent deformations. It is very probable, and the assumption is confirmed by experiment, that the magnetization in very rapid changes of field does not attain this region, while the molecules within the region of the constant μ can follow far more rapid oscillations than those here used. Further experiments, which will perhaps best be made by discharges of condensers, must decide this point.—*Wiener Berichte,* March 1, 1894.

RING-ELECTROMAGNET FOR PRODUCING STRONG FIELDS.
BY H. DU BOIS.

The large ring employed, made of the best Swedish iron (50 cm. mean diameter, 10 cm. thickness), is slit radially in one place, tangentially in another, so that the width of the former air-gap may be conveniently varied. It bears 12 coils, each having a resistance of 0·2 ohm and covering $20°$ ($\frac{1}{18}$) of the circumference; by means of these a maximum magneto-motive force of 108,000 ampere-turns may be applied, requiring about 6·5 horse-power; the highest value of the inductance is about 180 henries, corresponding to a "time-ratio" of $180/2\cdot4=75$ seconds; the mean values are of course less. Ballistic measurements are none the less out of the question.

When provided with flat pole-pieces the apparatus represents the simplest possible type of magnetic circuit, and is therefore well suited for an experimental verification of its laws. By a special method, which is described *in extenso,* the author was able to verify his form of the theory of magnetic circuits (Phil. Mag. Nov. 1890; Wied. *Ann.* xlvi. p. 491, 1892) with sufficient approximation. The leakage was roughly determined by a compass; its absolute amount was found to reach a maximum for a comparatively low magnetizing current, and to *diminish* considerably as the current was increased. This final decrease of leakage, which of course is more marked still when referred to unit flux of induction through the circuit, was previously found with a smaller ring by H. Lehmann (Phil. Mag. April 1893) and discussed by the author ('The Electrician,' xxix. p. 450, 1892). It was explained how this simple fact constitutes an "experimentum crucis" against the fallacy of assuming—arguing from analogy with a voltaic battery immersed in an electrolyte—that leakage must always increase when saturation is being approached. It was also found that leakage is considerably diminished by the ampere-turns near upon the air-gap: the "pole-coils" producing them fulfil the useful function of keeping the flux of induction together, thus preventing the lines from spreading.

The principal object of the apparatus is the production of strong fields by concentrating this flux through properly shaped pole-pieces. A theory of the latter was developed almost simultaneously (1888) by Stefan and Ewing and Low, in which the

assumption of absolute saturation is made. As this condition can never be fulfilled in practice, the author redetermined the best shape for the poles in an empirical way. It was found—in good agreement with Prof. Ewing's prediction—that it is best to take a straight truncated cone of semi-vertical angle 60° (instead of the theoretical 54° 44'). The field obtainable in air with such pole-pieces falls short of the theoretical value by several thousand units; however, it beats the previous record (about 30,000 C.G.S.) by a considerable amount. It was found—

$$\text{For } a = 5 \text{ mm.}; \quad H = 36,800 \text{ C. G. S.}$$
$$\text{,, } a = 3 \text{ mm.}; \quad H = 38,000 \quad \text{,,}$$

where a denotes the diameter of the small truncated faces.

To give an idea of this field the author points out that a bit of good thin iron wire would easily get saturated up to $I = 1750$, corresponding to an induction

$$B = 38,000 + 4\pi \times 1750 = 60,000 \text{ C.G.S.}$$

This corresponds to a tension of $B^2/8\pi$ dynes per cm.², or 144 Kg-weight per cm.² A concentrated aqueous solution of ferric chloride in a U-tube (Quincke) would be lifted about half a metre; finally, the resistance of a bismuth spiral would be nearly trebled in the field.

The author concludes that it is possible to obtain fields of, say, 40,000 C.G.S. with ring-electromagnets of reasonable size; but that stronger fields can probably only be reached by means out of all proportion with the purpose in view.—Wiedemann's *Annalen,* li. p. 537 (1894).

ON THE THERMAL BEHAVIOUR OF LIQUIDS.

To the Editors of the Philosophical Magazine.

Gentlemen,

The last number of your Journal contains a paper by Messrs. Ramsay and Young, to which it would not be necessary to reply if all your readers were familiar with the investigations on the thermal behaviour of liquids. But as this cannot be assumed to be the case, I am for the sake of my scientific reputation compelled to reply.

Messrs. Ramsay and Young reproach me with an error of observation of about 50° in the determinations of the critical point; as these authors well know, it would be impossible even for the most inexperienced to make so serious a mistake. The liquid I used had really the critical temperature stated, but I was in error in relying upon the statement of the chemist who supplied me, that the products were pure.

The error is acknowledged by myself in the book I published, and the critical temperatures I found are no longer given. But it is too much to assume that a physicist who once in a way had the misfortune to work with a mixture instead of a pure substance, has become incapable of making a correct observation.

Liége, May 7, 1894. P. DE HEEN.

INDEX to VOL. XXXVII.

END OF THE THIRTY-SEVENTH VOLUME.

Nickel Wire
$l = 19 \cdot 4 \, cm$
$d = 2 \cdot 04 \, mm$

Fig. 5.

Solenoid

Fig. 4.

Nickel Wire
$l = 19 \cdot 4 \, cm$
$d = 2 \cdot 04 \, mm$

Fig. 6.

Fig. 1.

Fig. 2.

Nickel Wire
l = 19·4 cm
d = 2·04 mm
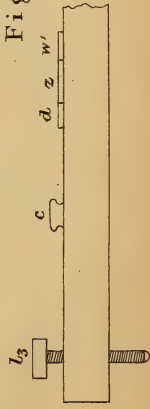
Fig. 5.
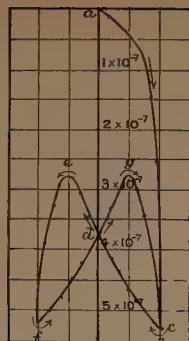
Front

Fig. 3.

Back
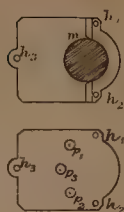
Nickel Wire
l = 19·4 cm
d = 2·04 mm

Fig. 7.

Solenoid
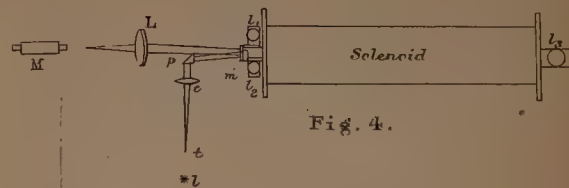
Fig. 4.

Nickel Wire
l = 19·4 cm
d = 2·04 mm

Fig. 6.
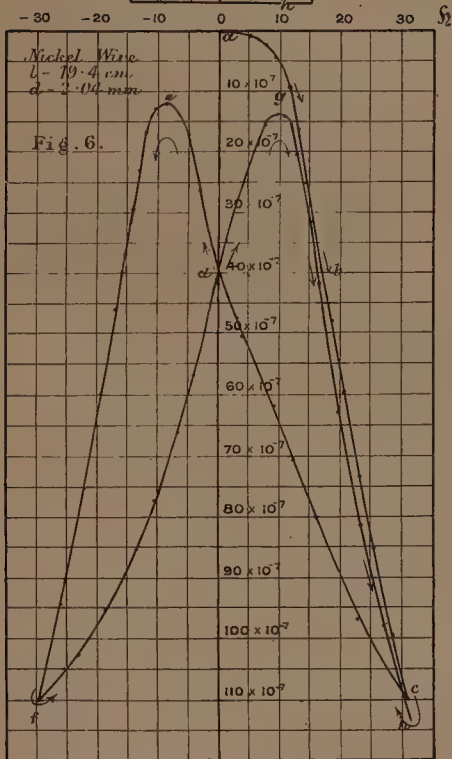
Nickel Wire
l = 10·0 cm
d = 2·04 mm

Fig. 8.

Fig. 1.

Fig. 2.

Mintern Bros. lith.

Fig. 2.

Iron Wire
l = 19·4 cm
d = 2·83 mm

Relation of polarization to current strength for various partitions in 30 % H₂SO₄

Current Strength : one division equals $\frac{1}{1000}$ Ampère.

#0 Gold

#1 Platinum

#2 Gold

#2 Platinum

#6 Gold

$\frac{1}{100}$ volt.

250

50

0

50

100

150

200

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Relation of polarization to current strength for various partitions in 30 % H₂ SO₄

Polarization upon the partition: one division equals $\frac{1}{100}$ volt.

#0 Gold
#1 Platinum
#3 Gold
#5 Gold
#2 Platinum
#6 Gold

Current Strength: one division equals $\frac{1}{1000}$ Ampère

Fig. 2.

250

200

Polarization upon the partition: one division equals $\frac{1}{100}$ volt.

150

100

50

0

me: one division equals two minutes

50   100   150

SO_4 unaffected by the passage of the current:
ent closed during dotted intervals.

mean of all of Table VII

one selected series

Fig. 3.

Relation of
strength,

#6 GOLD

: one division equals one degree centigrade.

24°   29°   34°   39°   44°

efficient of "critical current" in Sodium Acetate

Fig. 1.

Polarization upon the partition: one division equals ten volts

0.15 Ampère
0.10 Ampère
0.05 Ampère
0.04 Ampère
0.03 Ampère
0.02 Ampère
0.01 Ampère

Thickness of the partitions: one division equals $\frac{1}{50000}$ mm.

6 GOLD   # 5 GOLD   # 3 GOLD

Relation of the polarization to the thickness of the partition for a given current strength, in 30 % H_2SO_4.

Fig. 2.

Or passed the partition: one division equals 1000 gramme

Time: one division equals two minutes

Diffusion of $CuSO_4$ unaffected by the passage of the current: current closed during dotted intervals.

Critical current: one division equals $\frac{1}{100}$ Ampere

mean of all of Table VII
one selected series

Fig. 3.

Temperature: one division equals one degree centigrade

Temperature coefficient of "critical current" in Sodium Acetate solution.

Wind velocities recorded July 16, 1887, at the Allegheny Observatory, with a
Robinson anemometer registering every 25 revolutions.

Abscissae = Time.
Ordinates = Wind velocities in miles per hour.

Wind, S.S.E.; Weather, cloudy.
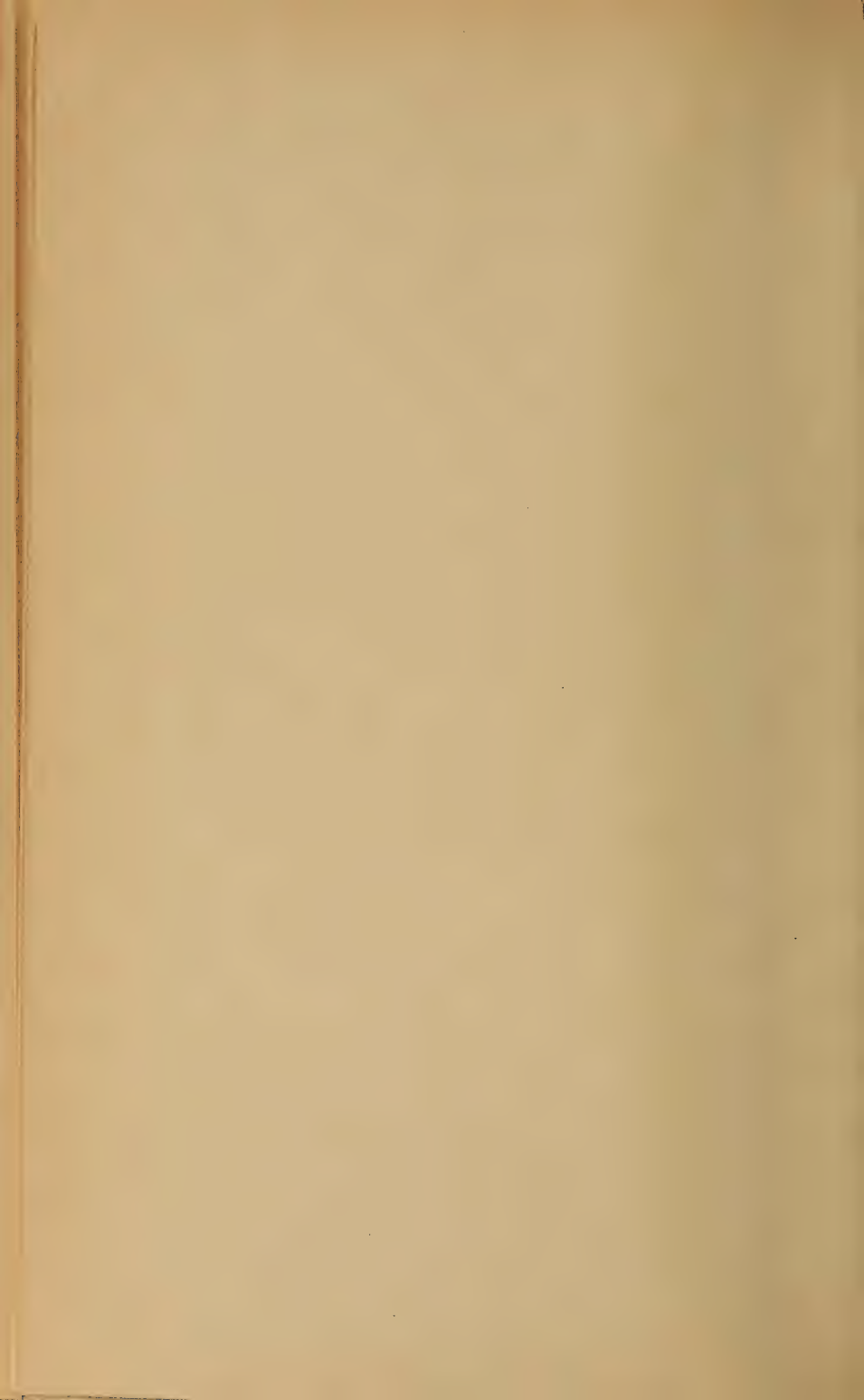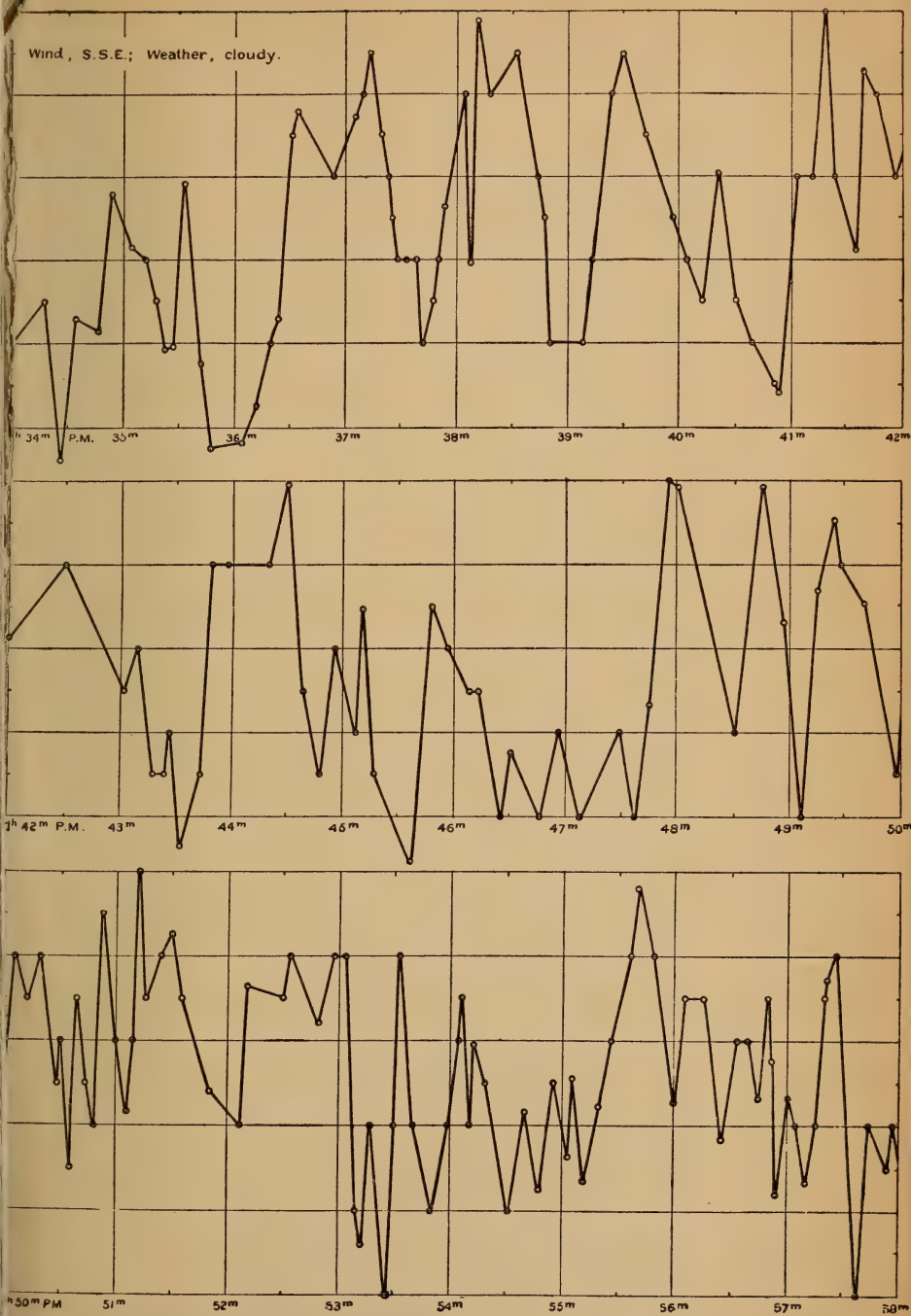
Wind velocities recorded January 14, 1893, at the Smithsonian Institution, with a light
Robinson anemometer (paper cups) registering every revolution.

Abscissae = Time.

Ordinates = Wind velocities in miles per hour.

Wind velocities recorded February 4, 1893, at the Smithsonian Institution, with
a light Robinson anemometer (paper cups) registering every revolution.

Abscissae = Time.

Ordinates = Wind velocities in miles per hour.
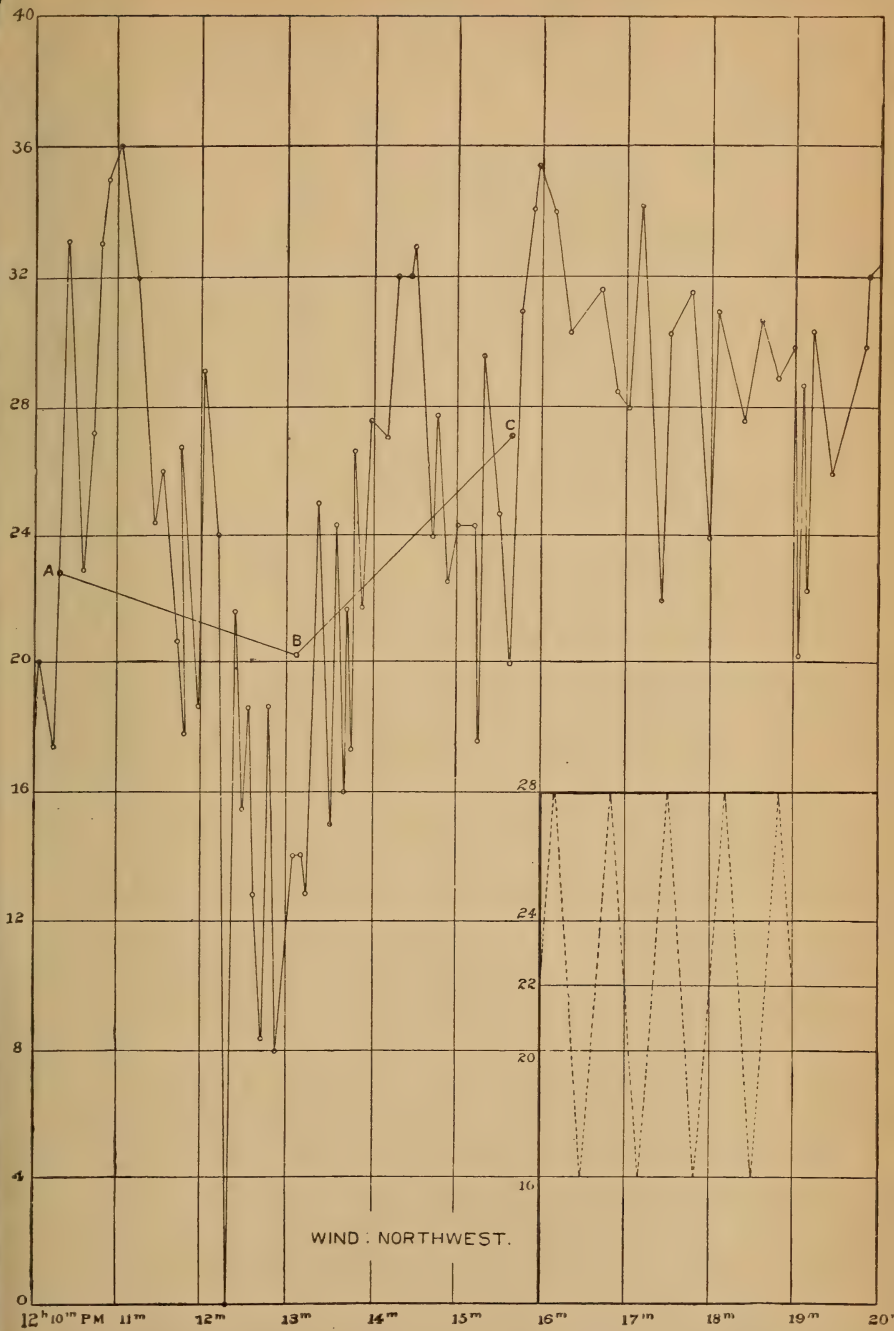
Wind velocities recorded February 4, 1893, at the Smithsonian Institution, with a light Robinson anemometer (paper cups) registering every revolution.

Abscissae = Time.

Ordinates = Wind velocities in miles per hour.
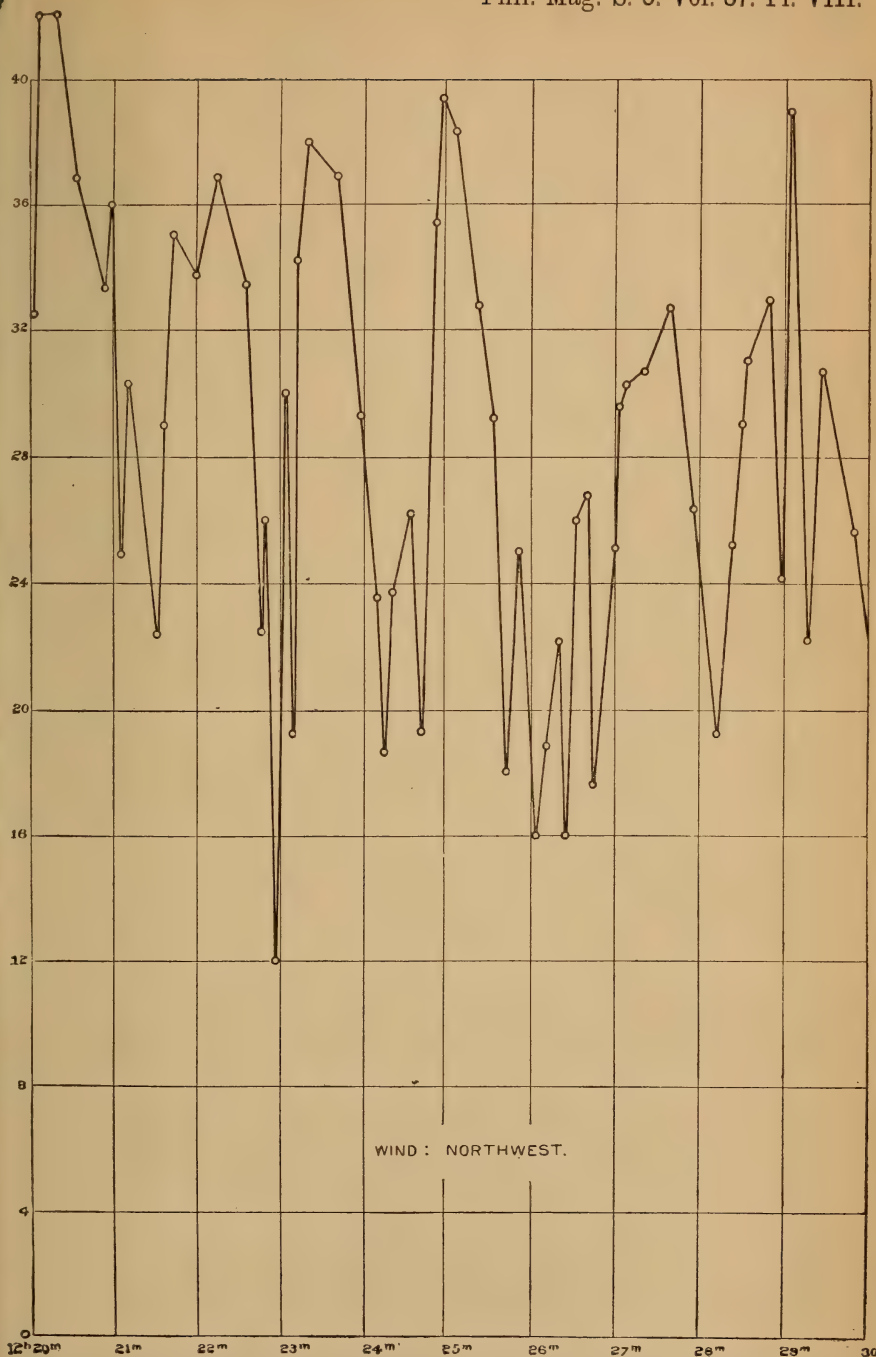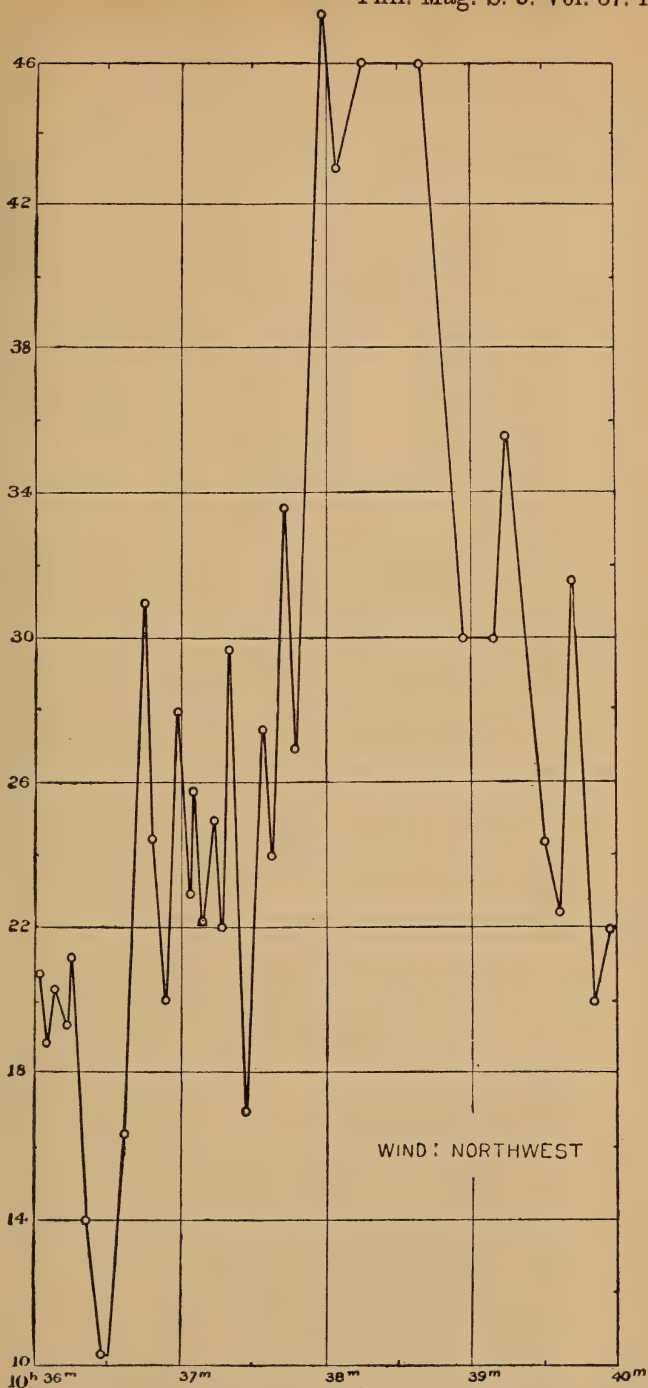
Wind velocities observed at Smithsonian Institution, February 20, 1893, with a Robinson anemometer (aluminum cups) registering every five revolutions.

Abscissae = Time.
Ordinates = Wind velocities in miles per hour.

Curves showing the ratios (expressed as a percentage) of the impedance of current in

Frequency.

Values of α.

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Curves showing the ratios (expressed as a percentage) of the impedance of, current in, magnetizing effect of, & power impressed on, the primary when the secondary is short circuited, to the same when the secondary is on open circuit.

III. Impedance curve.   GGG. Magnetising curve.
CCC. Primary current curve. PPP. Power curve.

Percentage ratios.

Frequency.

Values of α.

Values of α.

100

90

80

70

60

50

40

30

20

10

0

Values of mean power.

Curve P is power impressed on the primary.
  „   H is heat power developed in the primary.
  „ P_2 is power developed in the secondary.
      For all these three curves the
      secondary is short circuited.
Curve P_1 is power impressed on the primary when
      the secondary is open.
$\frac{E^2}{2r_1}$ is taken as equal 100
Point A where curves P & P_1 cut is for $\alpha = \frac{1}{\sqrt{2}}$
Point B   „   „ P_1 & H „   „   „ $\alpha = \sqrt{2}$.

P_1

P

H

A

P

P

H

P_1

H

B

H

P_2

P_2

P_1

P_2

P_2

.2   .4   .6   .8   .1   1.2   1.4   1.6   1.8   2

Values of α .

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